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TRANSACTIONS of the BOSE RESEARCH INSTITUTE CALCUTTA

Vol. X, 1934–1935

BIOLOGICAL AND PHYSICAL RESEARCHES

EDITED BY

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BIOLOGICAL AND PHYSICAL RESEARCHES

I.—INTRODUCTORY

BY

SIR J. C. BOSE, F.R.S.

A SYNOPSIS of various investigations carried out during the last year in different branches of biophysics, in anthropology and in advanced physics is given below.

The effect of age in modifying the internal physiological activities.—In this the variations induced in the Contractility, the Apex time, the Latent period and the Velocity of Transmission of Excitation in the conducting tissue of the plant have been exactly determined.

The effects of continuous and of intermittent illuminations on phototropism.—Special investigations that have previously been carried out at the Institute fully established the important discovery that, in regard to the photosynthetic action of light, intermittent illumination is, under certain circumstances, relatively more effective than continuous light. The particular modifying condition is the frequency of intermittence. In regard to phototropism also, the intermittent light is likewise found to be more effective than uninterrupted light. The relative efficiency of intermittent light, moreover, is at its maximum at a high frequency of intermittence. When the frequency of intermittence undergoes a decline, the effectiveness of intermittent light also exhibits a depression.

The effects of continuous and of intermittent lights on longitudinal growth.—Special devices for recording rates of longitudinal growth and for the production of intermittent lights of various frequencies were successfully employed.

It was found that the retardation induced in the rate of growth is, generally speaking, greater under intermittent illuminations than under continuous light. Even in regard to the relative efficiency of intermittent lights, quicker frequencies of intermission are found to be relatively more effective than those induced by slower frequencies. A wider generalisation is reached in regard to the action of continuous and interrupted lights on green plants. All diverse activities in these plants such as photosynthesis, phototropism and the activity of growth are found to undergo modifications which are essentially of a similar character.

Investigation on the 'after-ripening' of the seed led to the establishment of certain relations which existed between this particular process and the moisture content of the seed. It was found that there is an optimum condition of moisture content below or above which the period of germination undergoes a prolongation. The resting seed is, however, capable of immediate germination by absorption of water through a minute hole made by a pin prick. The time of germination which results from swelling by absorption of water is greater the lower the water content of the seed. But after the swelling has been attained, the actual time taken for germination is almost the same in all the seeds though they may have different moisture contents. It is certain conditions in the seed-coat that prevent the absorption of water during the resting stage. This factor which confers impermeability is not extended throughout the whole thickness of the seed-coat, but is most effectively present in the outermost layer of the testa. The percentage of moisture of the resting seed has an important bearing on the length of the after-ripening period; the period is considerably lengthened when the percentage of moisture is low.

The effect of variation of temperature on the respiration of a flower.—The respiratory activity is found to undergo a depression when the flower is subjected to the prolonged action of high temperature. The depression due to the time-factor has been successfully overcome by the employment of the *Respirograph* specially devised for the investigation in which the time required for each investigation is reduced to a minimum. The results obtained show that the initial effect of rise of temperature is an enhancement of respiratory activity, which increases with the rise of tempera-

ture till a maximum is reached at 52° C., this being the *critical temperature maximum.* Above this critical point the rate of respiration undergoes a marked decline till there is a total cessation of respiration at death of the organism, which occurs above 55° C. The seasonal variation has no effect on the critical temperature maximum, which therefore remains the same in plants grown either in summer or winter. The temperature coefficient of respiration for the flower is found to be fairly constant over a range from 32° C. to 52° C., the value of Q_{10} being approximately 1·65. At lower ranges of temperature than the above, the value of Q_{10} is comparatively higher, being as high as 2·1.

Chemical examination of the Indian medicinal plant Trichosanthes dioeca shows certain characteristic variations in the proportion of the mineral constituents present in the different parts of the plant. In the tubers there is a high percentage of the alkali K_2O, as also a high percentage of phosphoric acid. In the stem there is present a high percentage of lime and almost an equal proportion of K_2O and Na_2O. The leaf ash is characterised by the presence of a high percentage of silica and lime. In the fruit there is a very high percentage of K_2O and moderately high percentages of lime and phosphoric acid and very little of silica. In the roots the amount of nitrogen is only 0·9 per cent., while in the leaves it is as high as 4 per cent. The different parts of the plant contain a bitter principle. A chemical and physical examination of the soil suitable for cultivation of *Trichosanthes* has also been carried out. The carbon to nitrogen ratio in the soil is about 10 to 1. The soil fs silty and is also suitable for the growth of rice.

Examination of seeds of certain varieties of Meconopsis as source of oil and manure.—In this paper the quantities of oil obtained from different species of *Himalayan Meconopsis* seeds grown at high altitudes have been determined. The residues left after oil extraction have also been examined chemically by estimating the different constituents present in them, particularly the amounts of total nitrogen, phosphoric acid and alkali which are fairly high in every case. It has been possible to grow some of the species with advantage at somewhat lower altitudes. It was found that the oil yield from seeds of *Meconopsis Wallichii* grown at Darjeeling is fairly high, being about 44 per cent. of the seed weight.

The chemical and physiological investigations of presence of Vitamin C in certain substances in plants.—A rapid method for detection and estimation of Ascorbic acid has been employed, and its presence in the juices of Date Palm, Palmyra Palm and Cocoanut Palm quantitatively determined. Additional investigations established the stability of these juices even under fermentation. Anti-scorbutic property of the Cocoanut fruit has been established by physiological experiments on guinea pigs. The Ascorbic acid contents of different *Gurs* obtained by boiling Date Palm juice have been found to be very high. Indications have been found of the presence of a mannose dehydrogenase in the juices of the different Palms. The presence of certain thermo-labile protective agents for the Ascorbic acid in Cocoanut water has been established. Investigations on the transference of Ascorbic acid from water to the kernel and from the kernel into the growing embryo via the follicle have been carried out. That Ascorbic acid plays a very important part in the growth of the embryo has also been established by observing the growth of isolated embryo in an Ascorbic acid medium. It has been found that green Cocoanut fibre exerts a destructive action on Ascorbic acid. Investigations have also been carried out in regard to the stability of Ascorbic acid in the Cocoanut water and kernel in contrast with the instability of the Ascorbic acid present in the juice of *Citrus decumana.*

In the Department of Anthropology special studies have been carried out of the *Human remains from a Mālér cemetery.*

In the Department of Physics the following investigations have been carried out :

The Spectrum of Zinc at Different Stages of Ionisation.

The Absorption Spectra of the Alkali Halides and their Constituents in Solution.

Absorption Spectra of Zinc and Cadmium Halides in Vapour State.

II.—MODIFYING EFFECT OF AGE ON THE PHYSIOLOGICAL ACTIVITIES OF THE LEAF OF *MIMOSA PUDICA*

BY

S. C. DAS, M.A., AND B. K. PALIT, B.Sc.

THE problem of the variation in the physiological characteristics of plants brought about by age has attracted the attention of plant physiologists for a long time. In this connection the works of Hover and Gustafson and of Pope are of interest. The relation of the physiological activities with the age of the leaf was determined by these workers from the observed changes in the respiratory activity.

It was found by Hover and Gustafson[1] that in the leaves of Corn, Sorghum, Wheat and Oats, increase of age is attended with a preliminary decrease in the rate of respiratory activity, attaining a minimum at middle age, beyond which there was an increase.

Pope[2] performed respiration experiments with leaves of Barley and concluded that the rate of respiration, which was high in young Barley leaves, decreased in proportion to the rapidity with which the leaves matured. The same worker found that catalase activity, which was low in young Barley leaves, increased to a maximum at about the time of leaf maturity, beyond which there was a decline.

In determining the influence of age in modifying the physiological characteristics of the leaves, Hover and Gustafson and Pope experimented on the leaves present at a given time on the stem and considered them as constituting an age series, the leaf contiguous to the growing point being the youngest and the one most remote the oldest.

[1] J. M. Hover and F. G. Gustafson, 'Rate of Respiration as related to Age,' *Journ. Gen. Physiol.*, vol. x (1926), p. 33.

[2] M. N. Pope, 'Catalase Activity and Respiration in the Leaves of Growing Barley,' *Journ. Agr. Res.*, vol. xlvi (1933), p. 35.

In ascertaining the variation of physiological activities with the age of the leaf the subject was studied, as will presently be described, by quite a different method of investigation which appeared to have many advantages. We have for a long time been engaged in studying the variation in the inner physiological activities of *Mimosa pudica* under the influence of several factors such as the production of inflorescence as well as of other changes in the environment. The subject of inquiry in the present paper is the experimental determination of the modification of some of the most important inner activities of the plant induced by age. For this purpose experiments were undertaken for quantitative determination of the various aspects of irritability of the leaf organs.

The measurements related to :

1. The contractile activity of the pulvinus of the leaf as indicated by :
   - A. The Amplitude of responsive movement.
   - B. The rapidity of contractile movement constituting the Apex time.
2. The Latent period of the pulvinus.
3. The Conduction of transmitted excitation in the petiole of the leaf.

Additional variation in the method of inquiry was made in the choice of leaves of various ages. In the first method, we took successive leaves on the stem from above downwards as constituting the age series. In the second, observations were made with an identical leaf during its whole life cycle. The conditions of the two methods of investigation, though not of a quite identical nature, were as similar as could be reasonably expected. We thought it would be interesting to determine whether the indications given by these two independent methods on the effect of age in inducing modification of physiological activities are of an essentially similar kind.

Experimental Arrangement

Investigations were carried out with potted specimens of *Mimosa pudica*. Selected seedlings of the plant were for

this purpose planted in big earthen pots. The plants were irrigated with a measured supply of water every evening. The potted specimens were grown in a glass house admitting of free ventilation. Automatic records of the physiological activities were obtained with the Resonant Recorder, the frequency of the writer being, in the experiments of this series, adjusted to be 10 times per second. The petiole of the leaf to be experimented upon was attached to the shorter arm of the writing lever by means of a fine cocoon thread, the magnification employed being only 5 times. The experiments with different leaves were performed under strictly uniform conditions of light and temperature. The source of light employed for illuminating the plant was a 300 candle power incandescent lamp placed vertically overhead at a distance of 1 metre. The temperature of the plant chamber was maintained constant between 31° C. and 31·5° C.

For the purpose of the experimental determination with leaves of varying ages on the stem, the dates of appearance of successive leaf buds on the stem were noted. The age of any leaf was calculated from the period of time which intervened between the date of appearance of the bud and the date of the experiment. When the requisite number of leaves, say about 8, had appeared in the course of about a month and a half, automatic records were taken enabling the measurements of various indications of physiological activities characteristic of different ages of the leaf.

For facility of representation, the successive leaves commencing from the growing point downwards are numbered I, II, III, and so on.

Determination of Contractile Activity of the Pulvinus

The contractile activity of the pulvinus is measured by the Amplitude of responsive movement to a testing stimulus applied directly to the pulvinus. A second phase of the activity is determined from the rate of responsive movement. The time interval between the initiation of response and the attainment of maximum contractile limit is conveniently designated as the Apex time.

Experiment 1. *Determination of the Amplitude of*

responsive movement and the Apex time of the pulvinus of leaf I.—When the pulvinus of the topmost leaf is directly stimulated by an induction shock, the Amplitude of response is seen to be 44 mm. (fig. 1). The age of the leaf on the day of experiment was 5 days.

It will be further noted that the curve of response is very flat, the maximum contraction being completed in the

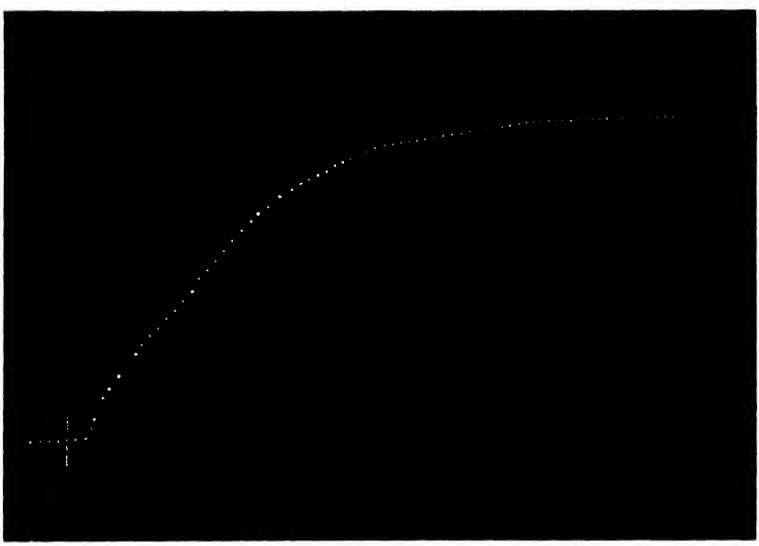

FIG. 1. Record of response of leaf I to direct stimulation. The Amplitude of response is seen to be 44 mm. Response is initiated at the second dot or 0·20 second after stimulation.

Maximum height is seen to be attained at the 60th dot or 6 seconds after initiation of response.

Successive dots in this and in the following records are at intervals of 0·1 second.

course of 6·0 seconds after its initiation (see fig. 1). The Apex time of the pulvinus of the youngest leaf of the series is therefore 6·0 seconds.

Experiment 2. *Determination of the Amplitude of responsive movement and the Apex time of the pulvinus of leaf II.*—On subjecting the second leaf from the growing point to the same intensity of stimulus, the Amplitude of response is seen to be enhanced to 66 mm.

(fig. 2). The age of this leaf on the day of experiment was 10 days.

In addition to the enhancement of Amplitude, the increase of physiological activity of the leaf is further seen from the erectile nature of the curve of response (see fig. 2). The Apex time is seen in this case to be 3·2 seconds.

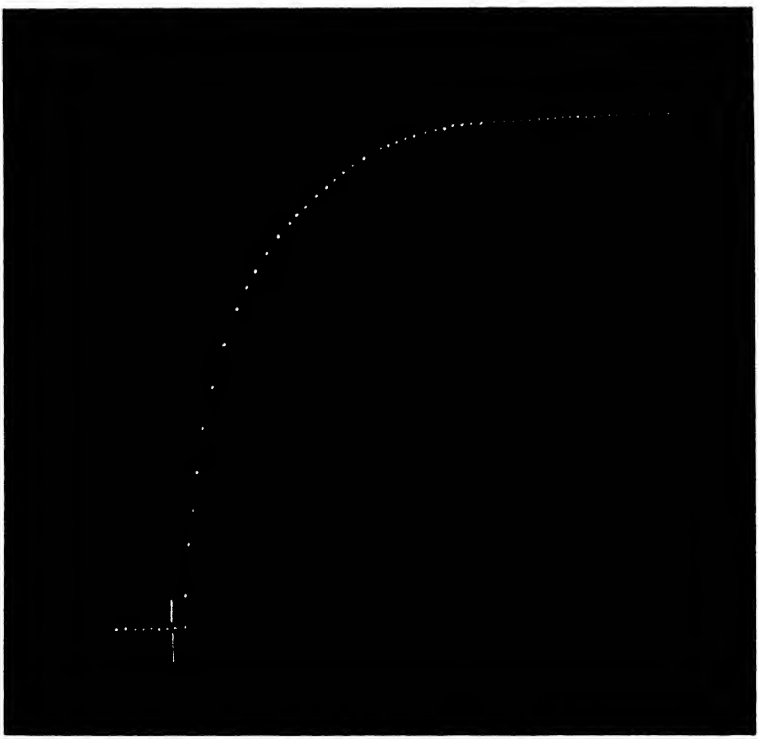

FIG. 2. Record of response of leaf II to direct stimulation. The Amplitude of response is 66 mm. Response is initiated 0·15 second after stimulation. Maximum height is attained at the 32nd dot or 3·2 seconds after initiation of response.

Experiment 3. *Determination of the Amplitude of responsive movement and the Apex time of the pulvinus of leaf III.*—The Amplitude of response is seen to be further enhanced with increase of age from 10 days in leaf II to 14 days in leaf III. The Amplitude of response is found to be 80 mm., the curve being considerably steep; the

maximum contraction was attained in the course of 2·0 seconds (fig. 3).

The Amplitude of response is seen to be maximum and the Apex time the shortest at this age of the leaf.

FIG. 3. Record of response of leaf III to direct stimulation. The Amplitude of response is 80 mm., while the Apex time is 2·0 seconds.

Experiment 4. *Determination of the Amplitude of responsive movement and Apex time of the pulvinus of leaf IV.*— In this leaf, which was 20 days old, the contractile activity undergoes slight diminution, the Amplitude of response being 72 mm. (fig. 4).

The Apex time also shows slight prolongation at this age of the leaf, the period being 2·3 seconds.

Experiment 5. *Determination of the Amplitude of responsive movement and Apex time of pulvinus of leaf V.*—The age of the leaf was 24 days. The contractile activity is

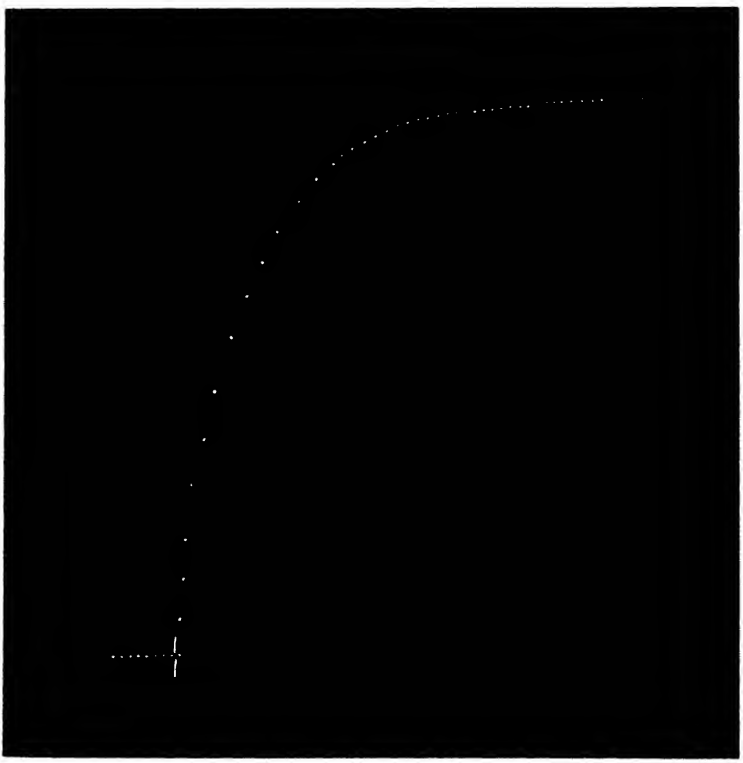

FIG. 4. Record of response of leaf IV to direct stimulation. The Amplitude of response is 72 mm., while the Apex time is 2·3 seconds.

found to be further diminished, the Amplitude of response being 65 mm. (fig. 5).

The period of maximum contraction also shows further prolongation, the Apex time being 2·8 seconds.

Experiment 6. *Determination of Amplitude of responsive movement and Apex time of pulvinus of leaf VI.*—In this leaf, 30 days old, the Amplitude of response is seen to have

undergone a marked diminution. The Amplitude is found in this case to be 55 mm. (fig. 6).

The Apex time is also seen to have become prolonged, the maximum contraction being completed in the course of 3·6 seconds.

Experiment 7. *Determination of Amplitude of responsive*

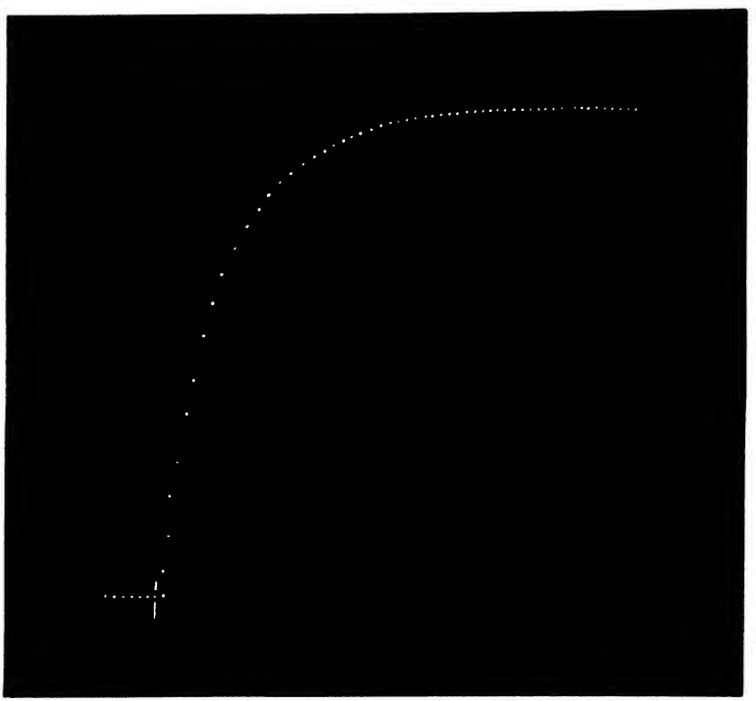

FIG. 5. Record of response of leaf V to direct stimulation. The Amplitude of response is 65 mm., while the Apex time is 2·8 seconds.

movement and Apex time of pulvinus of leaf VII.—With a still older specimen, which was 40 days old, the contractile activity shows a rapid diminution, the Amplitude of response being 42 mm. (fig. 7).

The Apex time also shows a considerable prolongation; the curve is less steep and the maximum height was attained in 4·6 seconds.

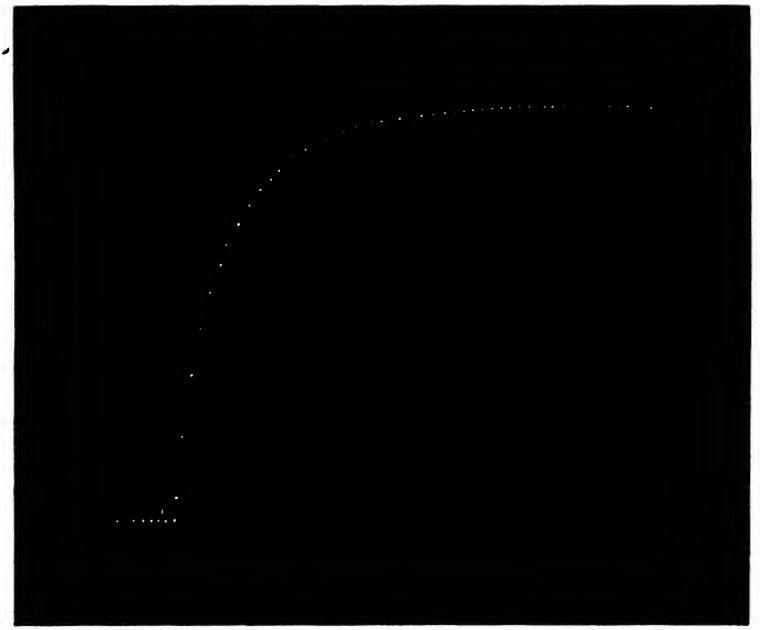

FIG. 6. Record of response of leaf VI to direct stimulation. The Amplitude of response is 55 mm., while the Apex time is 3·6 seconds.

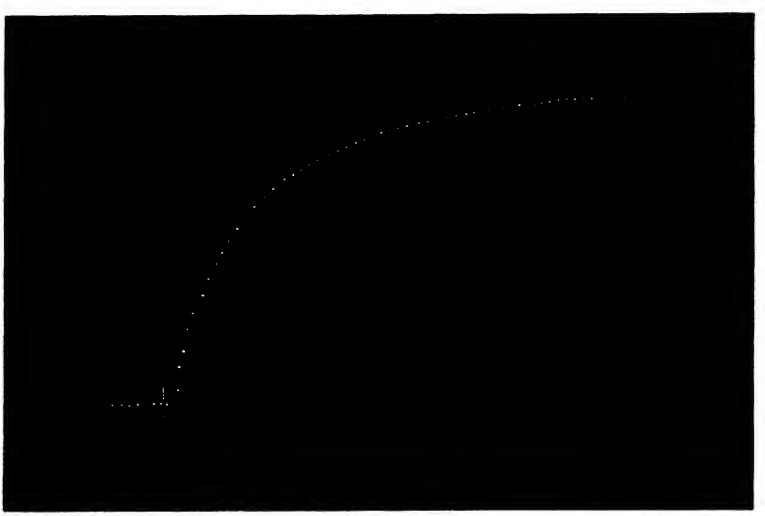

FIG. 7. Record of response of leaf VII to direct stimulation. The Amplitude of response is 42 mm., while the Apex time is 4·6 seconds.

TABLE I.—SHOWING AMPLITUDE OF RESPONSIVE MOVEMENT AND APEX TIME IN SPECIMEN 1

Leaf number	Age of leaf in days	Amplitude of contraction	Apex time in seconds
I.	5	44	6·0
II.	10	66	3·2
III.	14	80	2·0
IV.	20	72	2·3
V.	24	65	2·8
VI.	30	55	3·6
VII.	40	42	4·6

TABLE II.—SHOWING AMPLITUDE OF RESPONSIVE MOVEMENT AND APEX TIME IN SPECIMEN 2

Leaf number	Age of leaf in days	Amplitude of contraction in mm.	Apex time in seconds
I.	5	42	4·3
II.	9	58	2·8
III.	13	60	2·4
IV.	18	53	2·8
V.	23	50	3·3
VI.	27	47	3·6
VII.	32	38	4·5

TABLE III.—SHOWING AMPLITUDE OF RESPONSIVE MOVEMENT AND APEX TIME IN SPECIMEN 3

Leaf number	Age of leaf in days	Amplitude of contraction in mm.	Apex time in seconds
I.	6	50	3·5
II.	11	64	3·0
III.	15	66	2·0
IV.	19	57	2·2
V.	24	51	2·6
VI.	30	49	2·8
VII.	35	46	3·2
VIII.	41	37	3·4

In the tables on p. 14 are given data relating to the Amplitude of contractile movement and the Apex time of pulvinus as obtained from records of three typical specimens, 1, 2 and 3, of *Mimosa pudica.*

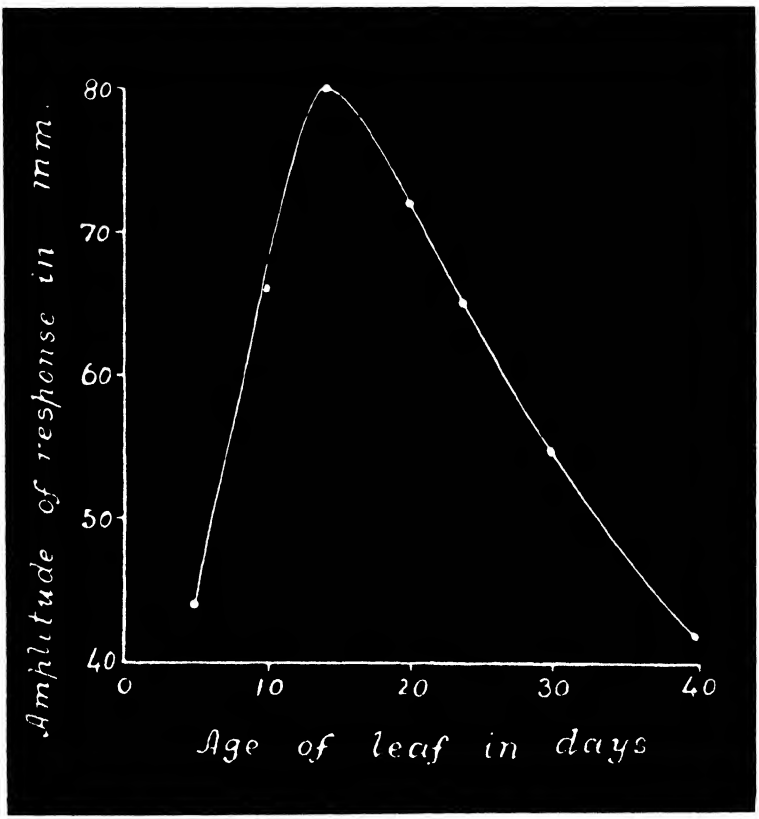

FIG. 8. Graphical representation of the variation of Amplitude of responsive movement with ages of successive leaves on the stem.

The ordinate represents the responsive movement in mm., while the abscissa indicates the age of leaves in days.

The curves in figs. 8 and 9 give graphical representation of the variation of Amplitude of responsive movement (fig. 8) and of Apex time (fig. 9) with ages of successive leaves.

Confirmatory results obtained in the two other specimens are given in Tables II and III.

It will be seen from the curves given in figs. 8 and 9 and Tables II and III that the Amplitude of contractile movement reaches a maximum which varies in different specimens between the ages of 13 and 15 days; with still

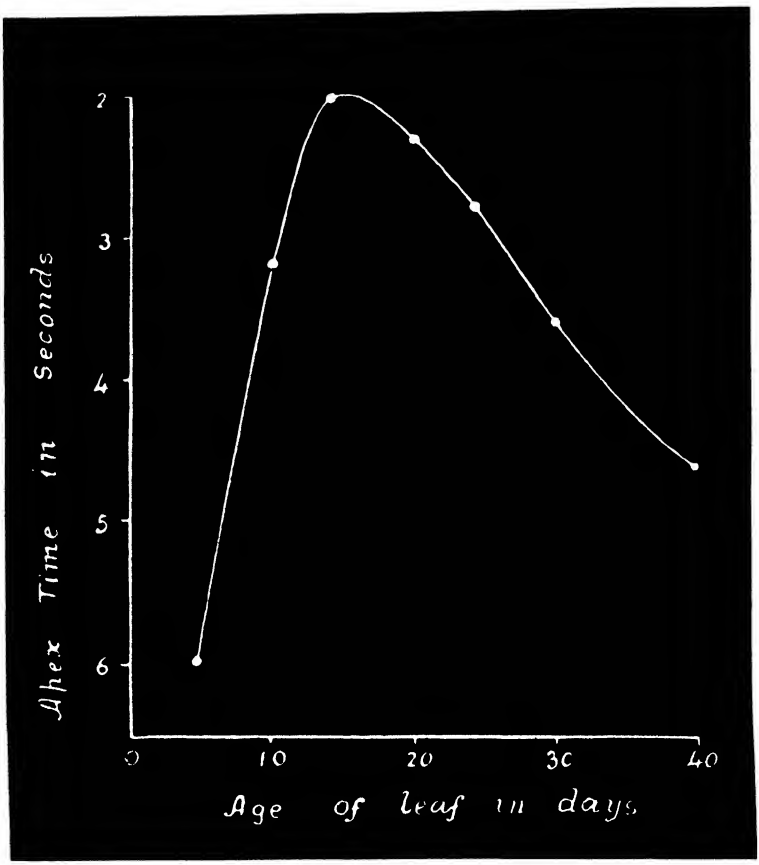

FIG. 9. Graphical representation of the variation of Apex time with ages of successive leaves on the stem.
The ordinate represents the Apex time in seconds, while the abscissa indicates the age of leaves in days.

older leaves there is a progressive diminution with the increase of age.

As regards the Apex time, it at first becomes increasingly shorter with the maturity of the leaf, the rapidity of

contraction being maximum between the ages of 13 and 15 days. With further increase of age, the Apex time is found to become gradually prolonged.

We next proceed to the determination of the effect of age in inducing variation of the Latent period in the successive leaves on the stem.

The Latent Period

When a motile organ such as the pulvinus of *Mimosa pudica* is stimulated directly by an induction shock, a short period elapses between the incidence of stimulus and the initiation of the responsive movement of the pulvinus. This time-interval is conveniently designated as the Latent period.

Experiment 8. *Determination of the Latent periods of the motile organ of successive leaves on the stem.* The records giving the Latent periods were obtained by means of the Resonant Recorder, the frequency of the writer being 10 times per second. For purpose of stimulation, one electrode of the induction coil was connected with the petiole of the leaf, the other electrode being in connection with the stem. The intervening pulvinus was thus directly stimulated; the intensity of the shock employed was 0·75 units.

It will be seen on reference to the records in figs. 1 to 7 that the Latent period of the pulvinus of the topmost leaf is 0·20 second (*cf.* fig. 1). This time-interval is seen at first to be progressively shortened with increasing ages of the leaf (*cf.* figs. 2 to 4), the Latent period being found to be at its shortest between the ages of 13 and 18 days of the leaf. Thus the shortest value of the Latent period is 0·05 second. Further increase of age is, however, attended by the prolongation of the Latent period, the value being 0·15 second when the ages of the leaf vary between 30 and 40 days (*cf.* figs. 5 to 7).

In Table IV are given the values of the Latent periods of pulvinus in three typical specimens of *Mimosa*.

The Latent period of the pulvinus is found from the tables on p. 18 to become shortened at first with increasing ages of the leaves, the shortest period being at ages varying from 13 to 18 days in different specimens. Still further increase of age is, however, attended by prolongation of the Latent period.

TABLE IV.—GIVING LATENT PERIODS OF PULVINUS OF A SERIES OF LEAVES ON THE STEM IN THREE SPECIMENS OF THE PLANT

Specimen 1

Leaf number	Age of leaf in days	Latent period in second
I.	5	0·20
II.	9	0·15
III.	13	0·05
IV.	18	0·05
V.	24	0·10
VI.	30	0·15
VII.	40	0·15

Specimen 2

Leaf number	Age of leaf in days	Latent period in second
I.	5	0·10
II.	9	0·10
III.	13	0·05
IV.	18	0·05
V.	23	0·10
VI.	27	0·15
VII.	32	0·20

Specimen 3

Leaf number	Age of leaf in days	Latent period in second
I.	5	0·15
II.	9	0·10
III.	14	0·05
IV.	18	0·05
V.	24	0·10
VI.	30	0·10
VII.	35	0·15
VIII.	41	0·15

The Conduction of Excitatory Impulse

Another special characteristic of the leaf of *Mimosa* is the possession of a conducting tissue in the petiole along which excitatory impulse is transmitted to a distance with a definite Velocity. It thus happens that a local stimulation initiated at any point of the petiole is conducted to the distant motile organ, the pulvinus, to cause its contraction with resulting fall of the leaf. The conducting power of the tissue is found from the Velocity of transmission of excitation in the petiole.

For the determination of the Velocity, automatic records were obtained with the Resonant Recorder, the electric stimulus of induction shock of moderate intensity of 0·75 unit being applied at a distance of 10 mm. from the pulvinus. The vibration frequency of the writer was 10 per second. The total time-interval T between the moment of application of stimulus and the initiation of response was determined from the record. Subtracting the Latent period L of the pulvinus under observation from the total time of transmission T, we get the true time of transmission t through the intervening length of petiole d. The Velocity V is determined from the formula :

$$V = \frac{d}{t} = \frac{d}{T - L}$$

The above method was employed for determination of Velocity of transmission of excitation in the petiole of different leaves of increasing ages commencing with the youngest near the apex of the stem. The uppermost leaf being abnormally thin and short could not be utilised for the determination, but the succeeding leaves numbered II to VII could be utilised for the purpose. It should be mentioned here that the determinations of the Velocity of transmission of excitation were carried out with the same leaves, of which the Amplitude of response, Apex time and Latent period had been previously determined and also described.

Experiment 9. *The Velocity of transmitted excitation in petiole of leaf II.*—The age of the leaf on the day of experiment was 9 days. The total time of transmission is seen from the record (fig. 10) to be 1·3 seconds. The

corresponding value of the Latent period of the pulvinus at this age of the leaf is 0·15 second (*cf.* fig. 2). The Velocity of transmission of excitation is therefore :

$$V = \frac{10}{1{\cdot}3 - 0{\cdot}15} = \frac{10}{1{\cdot}15} = 8{\cdot}7 \text{ mm. per second.}$$

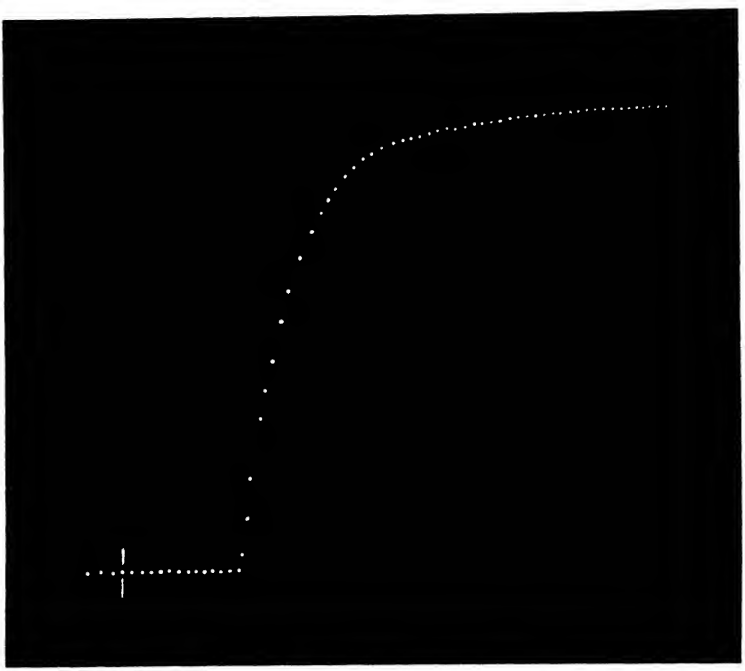

FIG. 10. Record for determination of Velocity of transmitted excitation in the petiole of *Mimosa pudica* in leaf II.
Stimulus was applied at the moment denoted by the vertical line in the horizontal portion of the record. Response is seen to be initiated at the 13th dot or 1·3 seconds after stimulation.

Experiment 10. *The Velocity of transmitted excitation in petiole of leaf III.*—The record (fig. 11) shows the total time of transmission to be 1·1 seconds. Taking into account the Latent period, the value of which is 0·05 second (*cf.* fig. 3), the Velocity is found to be 9·5 mm. per second. The age of the leaf on the day of experiment was 13 days.

Experiment 11. *The Velocity of transmitted excitation in*

petiole of leaf IV.—The total time of transmission is in this case seen to be 0·8 second (fig. 12). The Latent period, as will be found on reference to fig. 4, is 0·05 second. The Velocity of transmitted excitation is therefore 13·3 mm. per second in the petiole of leaf IV, which was 18 days old.

Experiment 12. *The Velocity of transmitted excitation in*

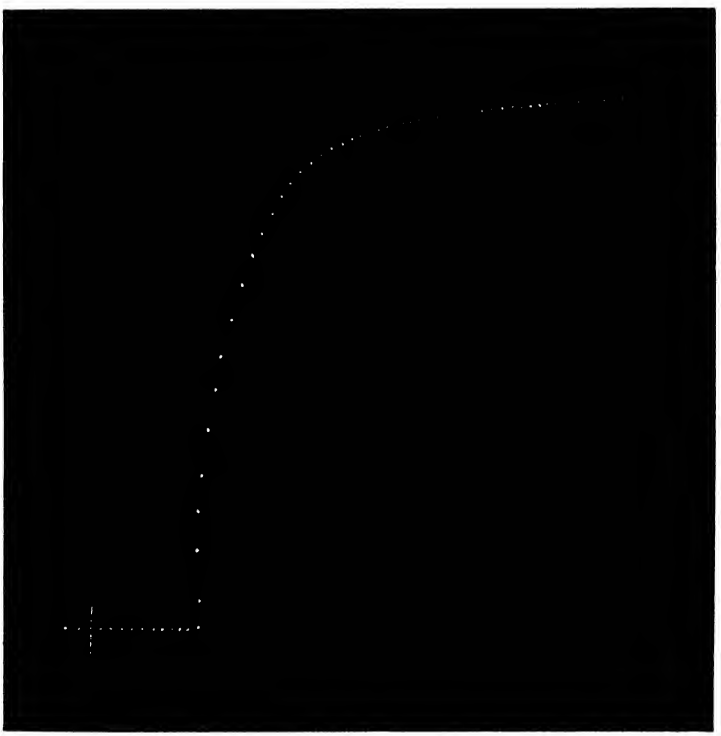

FIG. 11. Determination of Velocity of transmitted excitation in the petiole of leaf III.

petiole of leaf V.—In fig. 13 the response is seen to be initiated 1·2 seconds after the moment of stimulation, the leaf being 24 days old. Taking into account the Latent period of the pulvinus, the value of which is 0·10 second (*cf.* fig. 5), the Velocity is found from calculation to be 9·1 mm. per second.

Experiment 13. *The Velocity of transmitted excitation in petiole of leaf VI*.—The age of the leaf on the day of

experiment was 30 days. The total time of transmission is found to be 1·6 seconds (fig. 14). Subtracting from this the Latent period of the pulvinus, the value of which is 0·15 second (*cf.* fig. 6), the true time of transmission is 1·45 seconds. The Velocity is therefore 7·0 mm. per

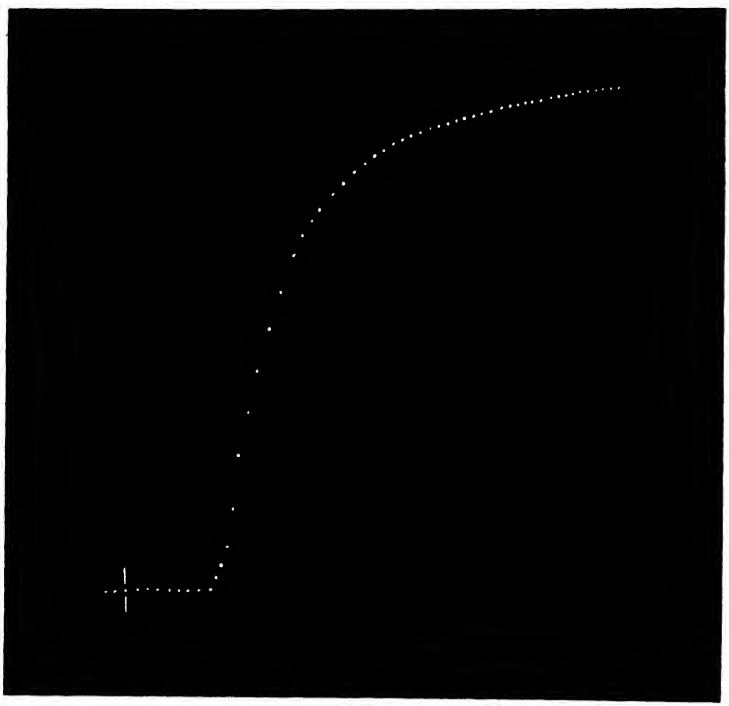

FIG. 12. Determination of Velocity of transmitted excitation in the petiole of leaf IV.

second, thus indicating a relative diminution in the speed of transmission.

Experiment 14. *The Velocity of transmitted excitation in petiole of leaf VII.*—The age of the lowermost leaf on the day of observation was 40 days. The total time of transmission is seen from the record (fig. 15) to be 2·1 seconds. The Latent period, as seen on reference to fig. 7, is 0·15 second. The Velocity of transmitted excitation is thus 5·1 mm. per second.

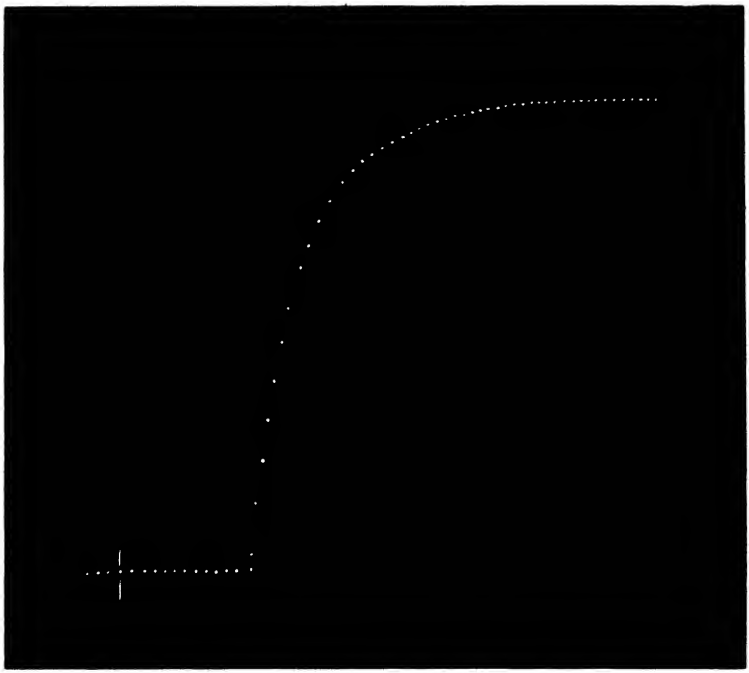

FIG. 13. Determination of Velocity of transmitted excitation in the petiole of leaf V.

The following table gives the data for Velocities of transmitted excitation in the petioles of successive leaves of increasing ages in specimen I of *Mimosa*.

TABLE V.—SHOWING VELOCITIES OF TRANSMITTED EXCITATION IN PETIOLES OF LEAVES OF INCREASING AGES

Specimen I

Leaf number	Age of leaf in days	Latent period in second	Total time of transmission in seconds	Velocity in mm. per second
II.	9	0·15	1·3	8·7
III.	13	0·05	1·1	9·5
IV.	18	0·05	0·8	13·3
V.	24	0·10	1·2	9·1
VI.	30	0·15	1·6	7·0
VII.	40	0·15	2·1	5·1

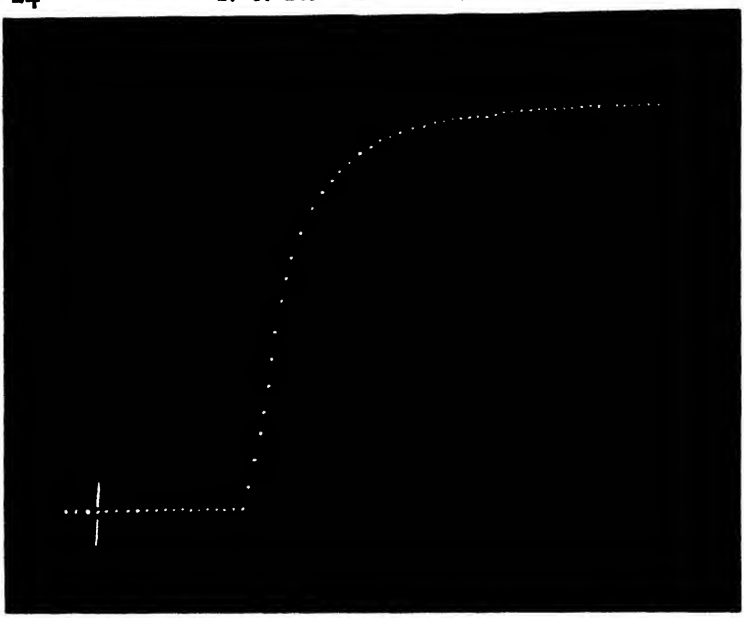

FIG. 14. Determination of Velocity of transmitted excitation in the petiole of leaf VI.

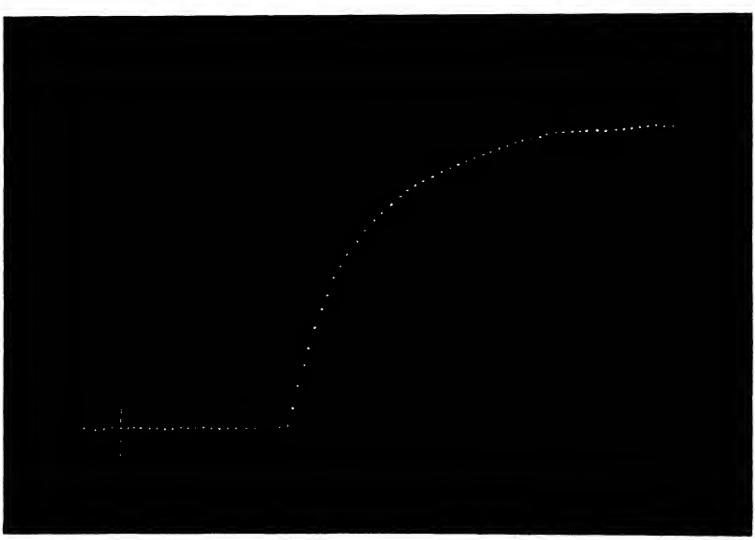

FIG. 15. Determination of Velocity of transmitted excitation in the petiole of leaf VII.

The Velocity of transmitted excitation in the second leaf from the growing point, 9 days old, is in this specimen seen to be 8·7 mm. per second. With older leaves lower down, the Velocity is seen at first to increase, reaching a

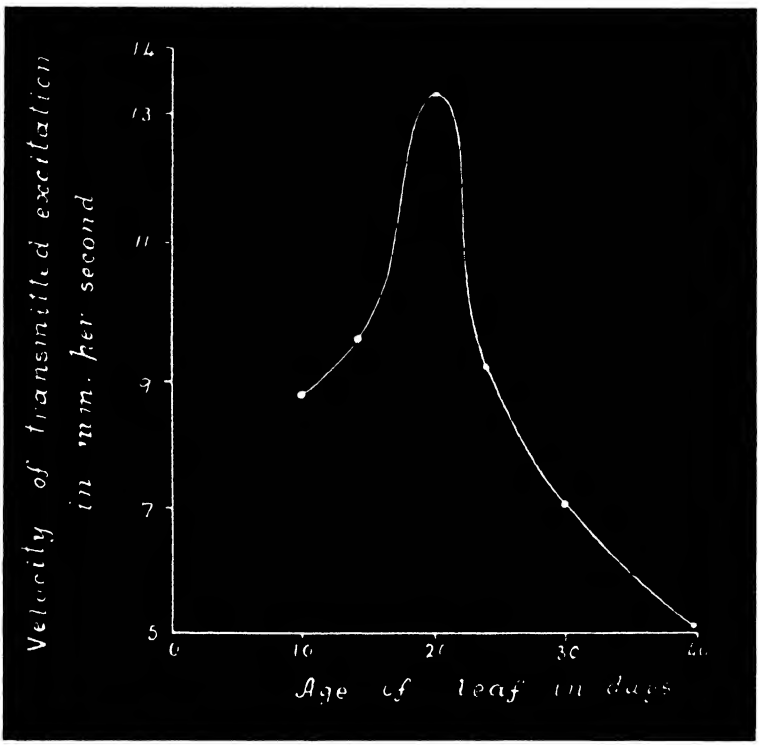

FIG 16. Graphical representation showing the relation between the Velocity of transmitted excitation in the petiole with the ages of successive leaves.

The ordinate represents the Velocity of transmitted excitation in mm. per second, while the abscissa indicates the age of leaf in days.

maximum at the age of 18 days of the leaf. Above this age the Velocity is found to be progressively diminished till it becomes as low as 5·1 mm. per second when the age of leaf is 40 days.

A graphical representation showing the relation between the Velocity of transmitted excitation in the petiole of leaf

with its age is shown in fig. 16, detailed data being given in Table V.

The two other specimens 2 and 3 give results (*cf.* Table VI) which practically confirm those given by specimen 1.

TABLE VI.—SHOWING VELOCITIES OF TRANSMITTED EXCITATION IN PETIOLES OF LEAVES OF INCREASING AGES

Specimen 2

Leaf number	Age of leaf in days	Latent period in second	Total time of transmission in seconds	Velocity in mm. per second
II.	9	0·10	0·70	16·7
III.	13	0·05	0·60	18·2
IV.	18	0·05	0·45	25·0
V.	23	0·10	0·65	18·2
VI.	27	0·15	0·85	14·3
VII.	32	0·20	1·30	9·1

Specimen 3

Leaf number	Age of leaf in days	Latent period in second	Total time of transmission in seconds	Velocity in mm. per second
II.	10	0·10	1·3	8·3
III.	14	0·05	0·6	18·2
IV.	18	0·05	0·7	15·4
V.	24	0·10	0·9	12·5
VI.	30	0·10	1·1	10·0
VII.	35	0·15	1·2	9·0
VIII.	41	0·15	1·45	7·7

It is now possible to describe the general results of numerous experiments that have been carried out. If we regard the series of leaves from the top downwards as constituting age series, it is found that the diverse physiological activities of the leaf attain their maximum value when the age of the leaf is between 13 and 18 days. Above this age, the activities undergo progressive enfeeblement with increasing age (*cf.* figs. 8, 9 and 16).

Physiological Variation induced in an Identical Leaf at Different Ages

Hitherto the effect of age was found from determinations made on different leaves, from above downwards, which constituted age series on the stem. We now undertook investigations on an identical leaf throughout its life cycle. For this purpose we chose a young leaf near the tip of a small plant and determined the changes of its physiological activities as it grew older and older. Precautions were taken to remove the side branches which made their appearance at the leaf axils, as they induced complications in the normal activity of the plant.

The experiment, as already stated, was carried out with the particular leaf which at the beginning happened to be growing at the top; it was continued with the same leaf at different intervals. The method of experimentation was the same as that with different leaves having different ages, the testing stimulus being of similar intensity.

Determinations of Amplitude and of Apex Time

Experiment 15. *Response of leaf when* 4 *days old.*— When the leaf was 4 days old it was stimulated directly by

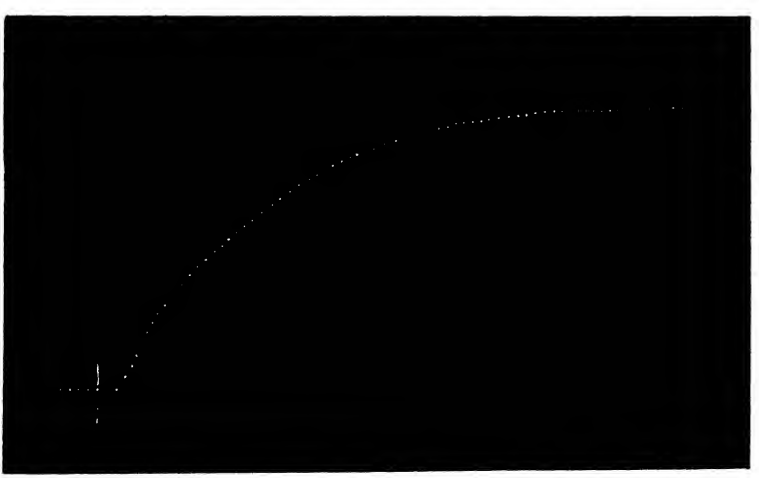

Fig. 17. Record of response of the leaf to direct stimulation when it was 4 days old.

an induction shock. The responsive contraction is comparatively feeble, the Amplitude of response being 37 mm. (fig. 17).

The enfeebled response is independently indicated by the flat slope of the curve. The maximum contraction was attained 6 seconds after the initiation of responsive movement (see fig. 17). The Apex time is therefore 6 seconds.

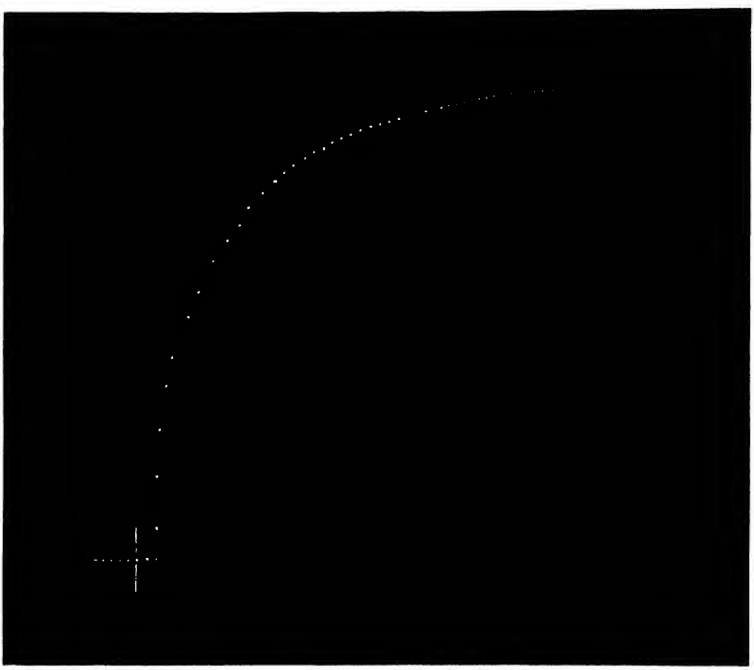

FIG. 18. Record of response of the leaf when 9 days old.

Experiment 16. *Response of leaf when* 9 *days old.*—The same leaf now exhibited a more vigorous response, the Amplitude being 62 mm. (fig. 18).

The Apex time is also found to be appreciably shortened, the period being 3·8 seconds.

Experiment 17. *Response of leaf when* 14 *days old.*—The Amplitude of response is seen to be further increased with advancement of age, the height of response being 65 mm. (fig. 19).

The Apex time also exhibits further shortening, the period being now 3·0 seconds.

Experiment 18. *Response of leaf when* 19 *days old.*—In experiment 17 it was found that when the leaf was 14 days old the Amplitude of response was 65 mm. and the Apex time 3·0 seconds. But when the leaf grew older (*i.e.* at 19 days), the physiological activity began to show decline.

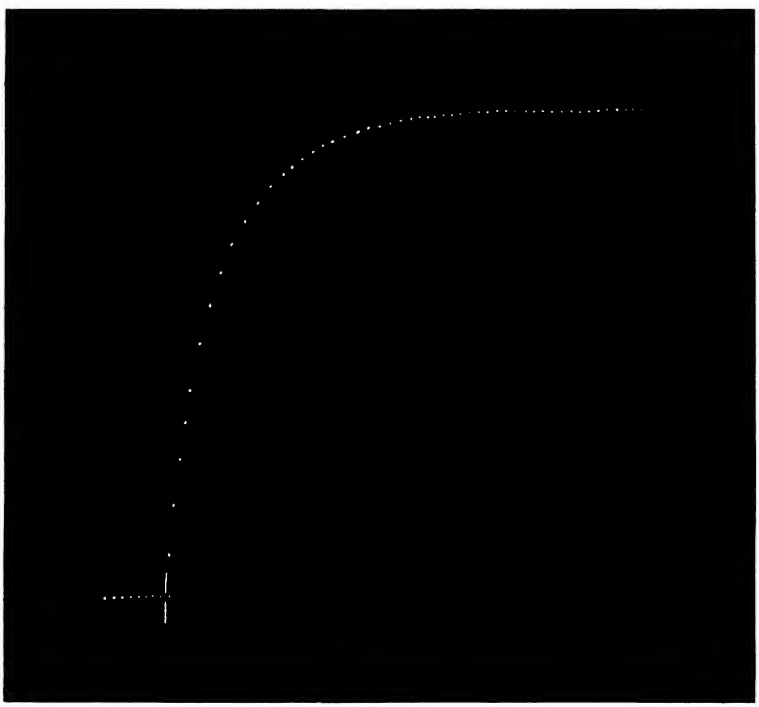

FIG. 19. Record of response of the leaf when 14 days old.

The Amplitude of response is now found to be 56 mm. (fig. 20).

The Apex time also becomes slightly prolonged, the period being 3·3 seconds.

Experiment 19. *Response of leaf when* 25 *days old.*—The Amplitude of responsive movement is seen to be 54·5 mm., while the Apex time is 3·4 seconds (fig. 21).

Experiment 20. *Response of leaf when* 29 *days old.*—

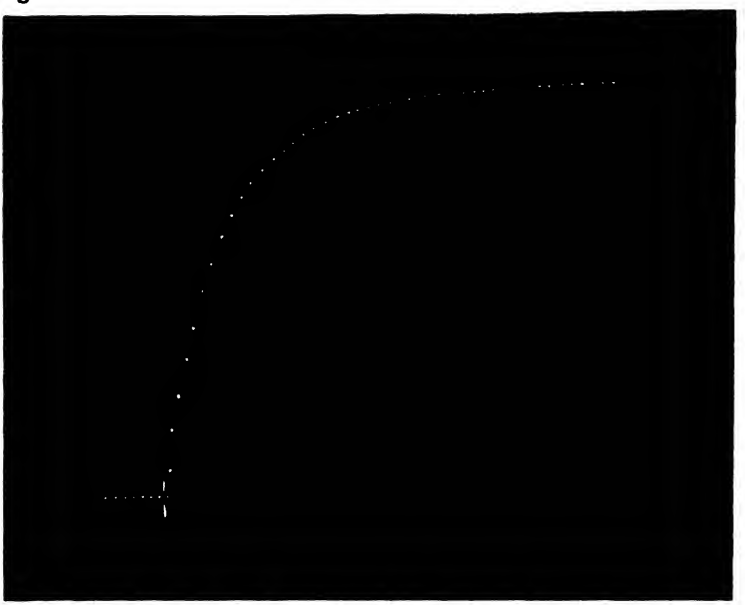

FIG. 20. Record of response of the leaf when 19 days old.

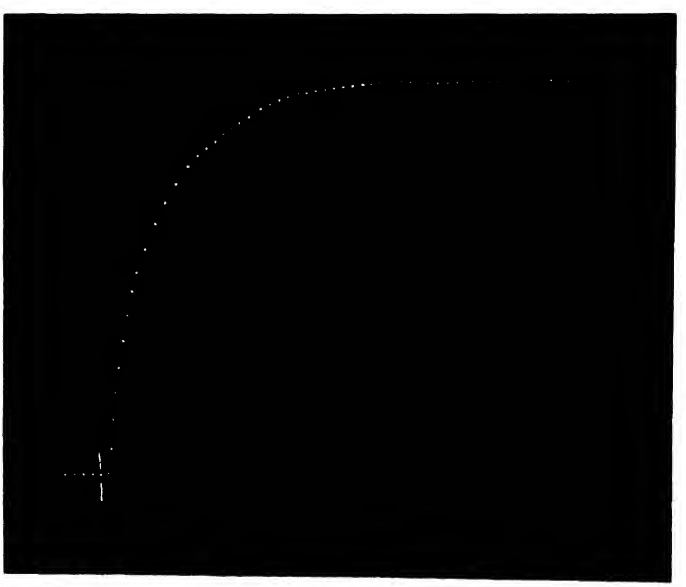

FIG. 21. Record of response of the leaf when 25 days old.

The contractile movement is seen to undergo only a slight diminution at this stage, the Amplitude being 54 mm. (fig. 22).

The Apex time is found to remain unaltered, the period being 3·4 seconds.

Experiment 21. *Response of leaf when* 39 *days old.*—The Amplitude of response now is 53 mm., while the Apex time is 3·5 seconds (fig. 23).

It will thus be seen that between the ages of 19 and 39

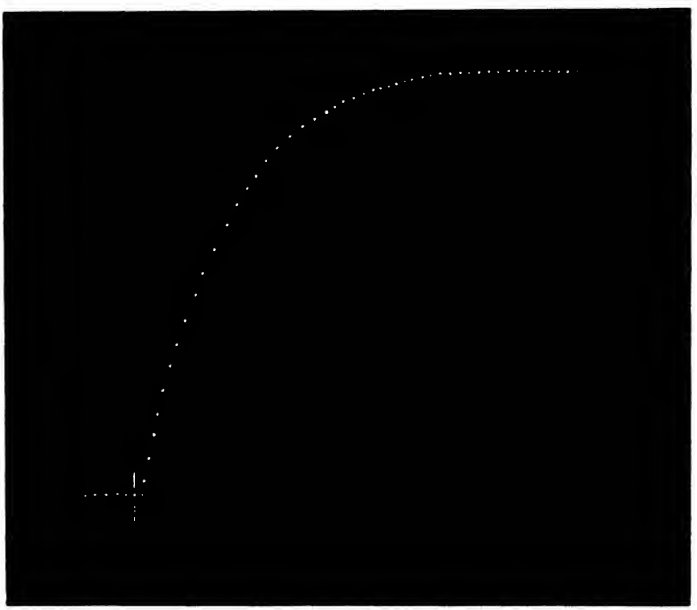

FIG. 22. Record of response of the leaf when 29 days old.

days there is but slight change in the physiological activity as indicated by Amplitude of response and Apex time.

Experiment 22. *Response of leaf when* 46 *days old.*—The last record of the series was taken when the leaf was older, namely 46 days. It is now found that the Amplitude of response and the Apex time have undergone a marked depression.

The height of responsive movement is now 40 mm.; moreover, the slope of the curve is very flat. The Apex time is found to be prolonged to 5·0 seconds (fig. 24).

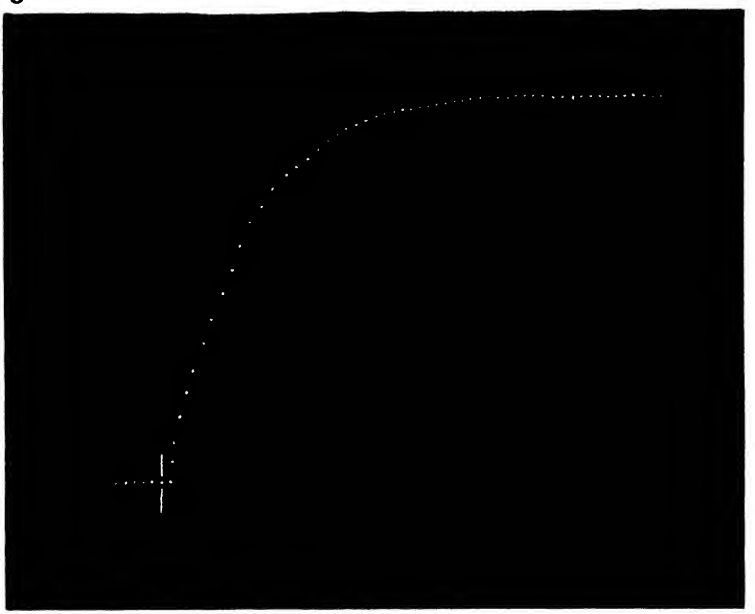

FIG. 23. Record of response of the leaf when 39 days old.

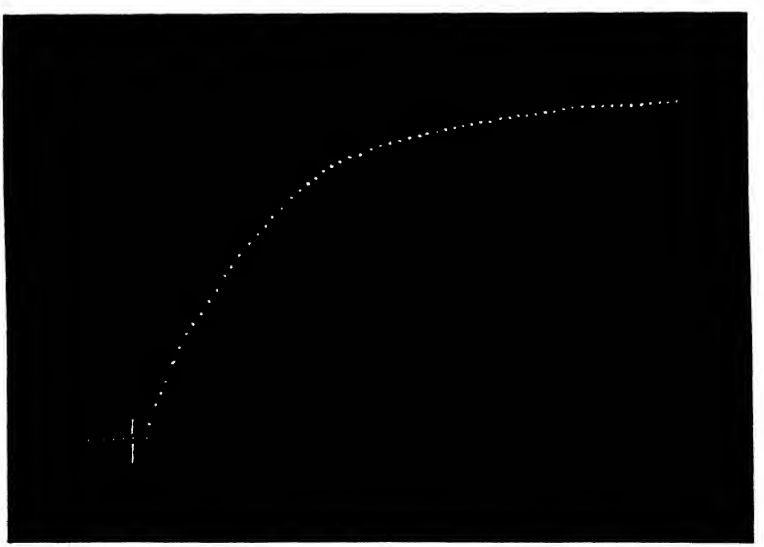

FIG. 24. Record of response of the leaf when 46 days old.

The following is a tabular statement of the experimental data showing the variation of Amplitude and of Apex time induced by the age of the leaf.

TABLE VII.—GIVING THE VARIATIONS OF AMPLITUDE OF RESPONSE AND OF APEX TIME INDUCED BY AGE

Specimen I

Age of leaf in days	Amplitude of contraction in mm.	Apex time in seconds
4	37·0	6·0
9	62·0	3·8
14	65·0	3·0
19	56·0	3·3
25	54·5	3·4
29	54·0	3·4
39	53·0	3·5
46	40·0	5·0

FIG. 25. Graphical representation of the relation between the Amplitude of response and the age of the leaf.
The ordinate represents the Amplitude of responsive movement in mm., while the abscissa indicates the age of the leaf in days.

The curves give graphical representations of the variation in the Amplitude of response (fig. 25) and of Apex time (fig. 26) at different ages of leaf in a typical specimen of *Mimosa pudica*.

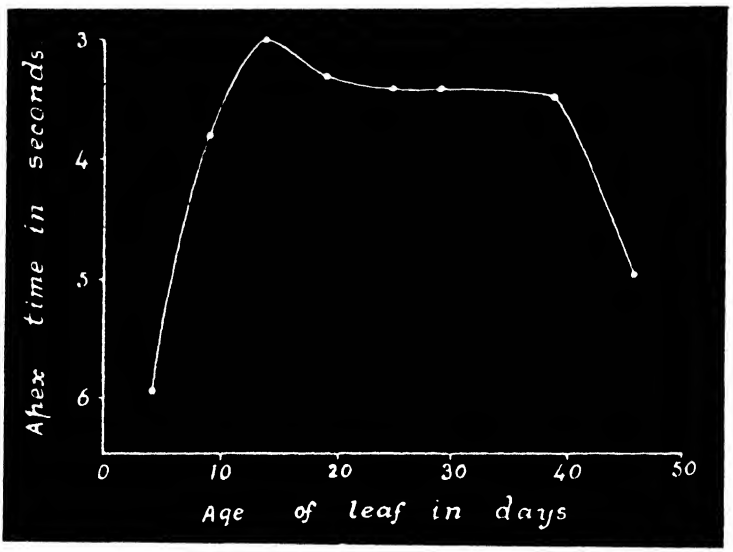

FIG. 26. Graphical representation showing the relation between the Apex time of the pulvinus and the age of the leaf. The ordinate represents the Apex time in seconds, while the abscissa indicates the age of the leaf in days.

TABLE VIII.—GIVING THE VARIATION OF AMPLITUDE OF RESPONSE AND OF APEX TIME INDUCED BY AGE

Specimen 2

Age of leaf in days	Amplitude of contraction in mm.	Apex time in seconds
4	39·0	5·0
9	57·0	3·0
15	61·0	2·6
20	54·0	2·8
27	53·0	2·8
37	52·0	3·0
43	36·0	3·8

Confirmatory results obtained with a second specimen are given in Table VIII.

It has already been shown (when the variation of contractile activity in relation to age of the leaf was obtained from *successive* leaves present on the stem as representing an age series), that the physiological activity showed an increase up to a particular age, and that beyond this age the activity underwent a progressive decline (*cf.* figs. 8 and 9).

In the alternative method, the increasing age of the leaf has been obtained by experimenting with an *identical* leaf at different intervals. This introduces conditions which are not exactly the same as those in which *different* leaves on the stem are regarded as constituting the age series. Nevertheless the general trend of experimental results obtained by the two different methods are fairly similar.

Thus referring to figs. 25 and 26, which gave results obtained with an identical leaf at different intervals, it is seen that the Amplitude of response increased till the leaf attained an age of 14 days. The Apex time also became increasingly shortened with advancement of age, the activity being maximum at the same age of 14 days of the leaf. After the attainment of maximum, both these activities are seen to undergo slight diminution up to 39 days of the age of the leaf. The activities then undergo a rapid diminution, as will be evident from the abrupt change of slope in the last portion of the curves (*cf.* figs. 25, 26).

Determination of Latent Period at Different Ages of the Leaf

The Latent period of the pulvinus, which is 0·20 second when the leaf is 9 days old (*cf.* fig. 18), is seen to become shortened with increase of age, reaching a minimum value of 0·05 second between the ages of 14 and 19 days of the leaf (*cf.* figs. 19, 20). It is then prolonged to 0·10 second when the age of the leaf is from 25 to 39 days (*cf.* figs. 21–23). With further advancement of age, the Latent period is prolonged to 0·20 second when the leaf is 46 days old.

The following table gives measurements of Latent period at increasing ages of the leaf in two typical specimens.

TABLE IX.—GIVING MEASUREMENTS OF LATENT PERIOD AT INCREASING AGES OF THE LEAF

Specimen 1

Age of leaf in days	Latent period in second
	0·20
	0·20
14	0·05
19	0·05
25	0·10
29	0·10
39	0·10
46	0·20

Specimen 2

Age of leaf in days	Latent period in second
4	0·25
9	0·20
15	0·10
20	0·15
31	0·15
37	0·15
43	0·20

Finally, the effect of age on the Velocity of transmitted excitation was determined at different ages of the particular leaf.

DETERMINATION OF VELOCITY OF TRANSMITTED EXCITATION AT DIFFERENT AGES OF LEAF

The Velocity of transmitted excitation along the petiole of leaf was determined with the identical leaf at intervals between the ages of 9 and 46 days. The local stimulation by induction shock was applied at a distance of 10 mm. from the pulvinus.

Experiment 23. *The Velocity of transmitted excitation in petiole of leaf when* 9 *days old.*—The transmitted excitation reached the pulvinus and caused excitatory fall of the leaf 1·8 seconds after the application of stimulus (fig. 27).

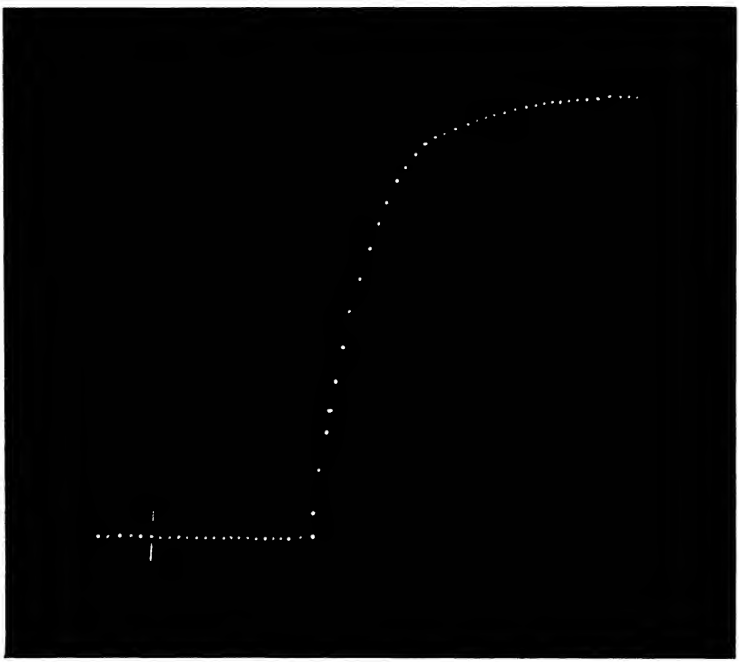

FIG. 27. Record for determination of Velocity of transmitted excitation in petiole of leaf when 9 days old.

Taking into account the Latent period of the pulvinus, which was found to be 0·20 second (*cf.* Table IX, Specimen 1), the calculated value of Velocity is 6·2 mm. per second.

Experiment 24. *Velocity of transmitted excitation in petiole of leaf when* 14 *days old.*—The responsive fall of the leaf occurred 1·10 seconds after application of stimulus (fig. 28). The Velocity, after making allowance for the Latent period, is found to be 10·6 mm. per second.

Experiment 25. *Velocity of transmitted excitation in petiole of leaf when* 19 *days old.*—Responsive fall of the leaf now occurred 1·45 seconds after application of stimulus

(fig. 29). The Velocity is in this case found to be 7 mm. per second.

Experiment 26. *Velocity of transmitted excitation in petiole of leaf when* 25 *days old.*—The period of transmission is now 1·75 seconds (fig. 30). Taking into account the Latent period, the Velocity is found to have undergone a diminution, namely, 6 mm. per second.

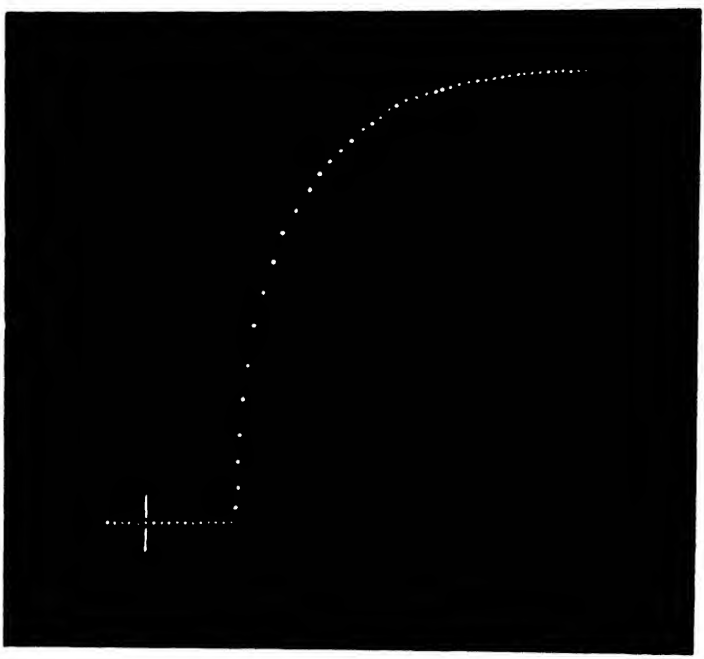

FIG. 28. Determination of Velocity of transmitted excitation in petiole of leaf when 14 days old.

Experiment 27. *Velocity of transmitted excitation in petiole of leaf when* 29 *days old.*—The responsive fall occurred 1·85 seconds after the application of stimulus (fig. 31). The Velocity of transmitted excitation is in this case still slower, namely, 5·7 mm. per second.

Experiment 28. *Velocity of transmitted excitation in petiole of leaf when* 39 *days old.*—The period of transmission is now 1·95 seconds (fig. 32). The Velocity is found after calculation to be 5·4 mm. per second.

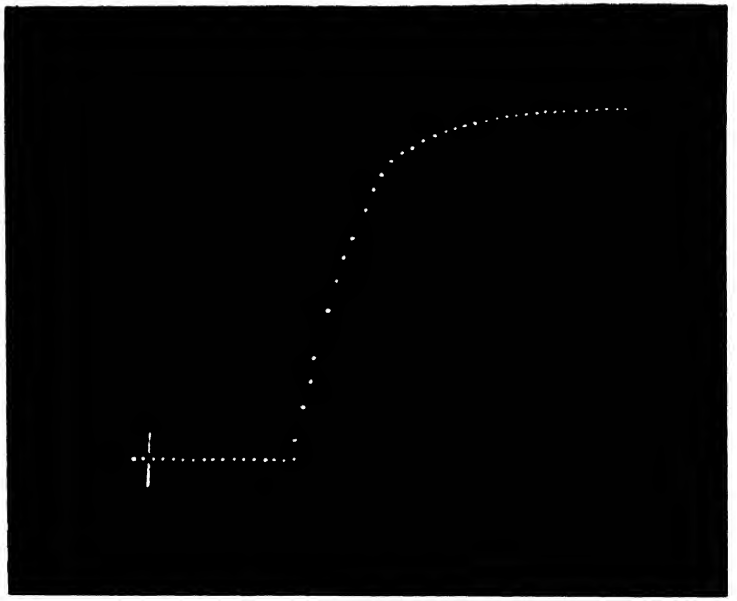

FIG. 29. Determination of Velocity of transmitted excitation in petiole of leaf when 19 days old.

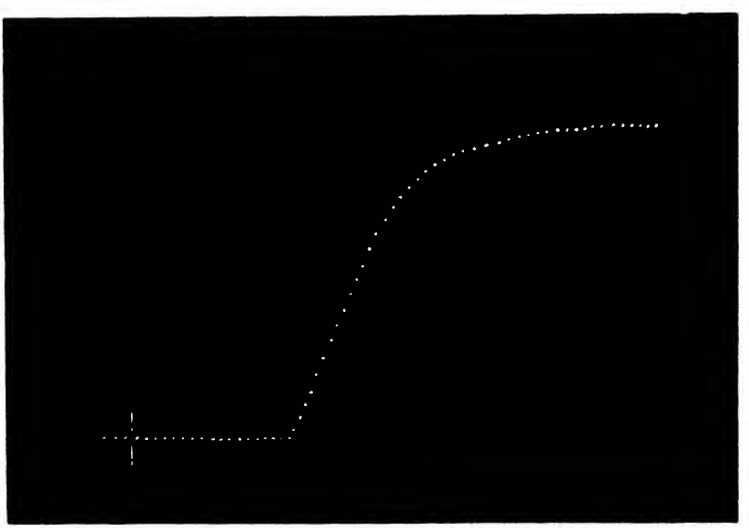

FIG. 30. Determination of Velocity of transmitted excitation in petiole of leaf when 25 days old.

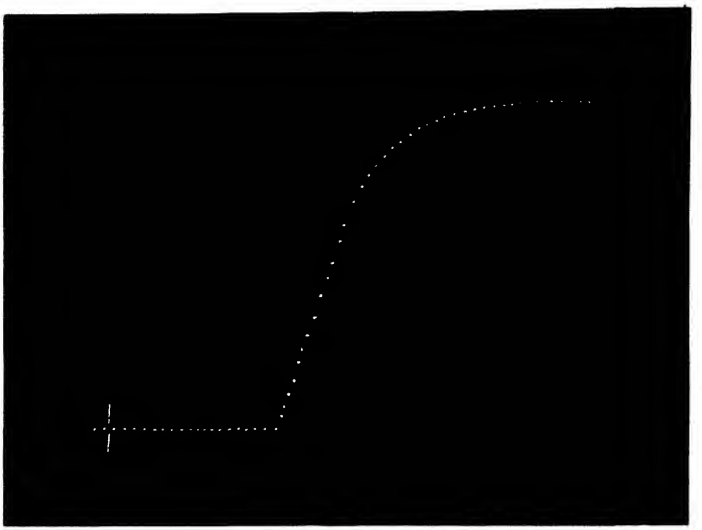

FIG. 31. Determination of Velocity of transmitted excitation in petiole of leaf when 29 days old.

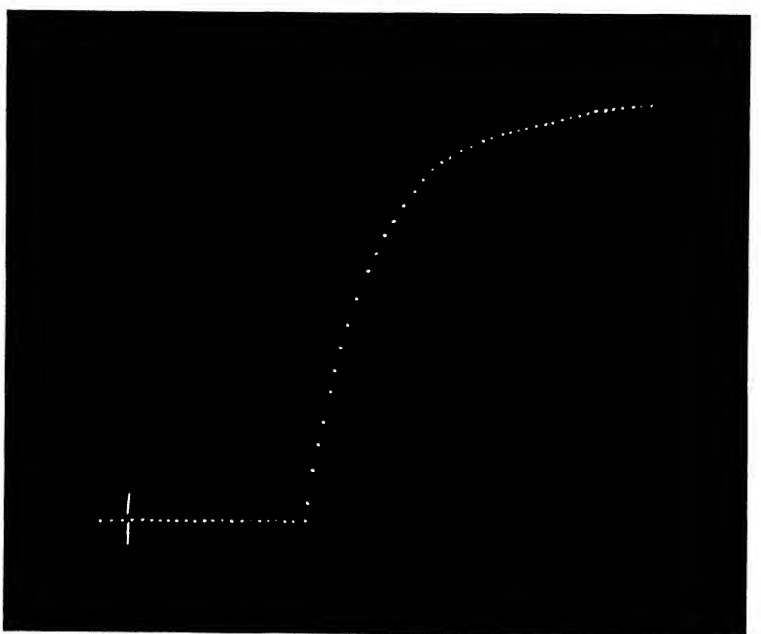

FIG. 32. Determination of Velocity of transmitted excitation in petiole of leaf when 39 days old.

Experiment 29. *Velocity of transmitted excitation in petiole of leaf when* 46 *days old.*—The speed of transmission is now seen to have become considerably slower, the excitatory fall of the leaf occurring 2·6 seconds after application of stimulus (fig. 33). The Velocity is found to be 4·2 mm. per second.

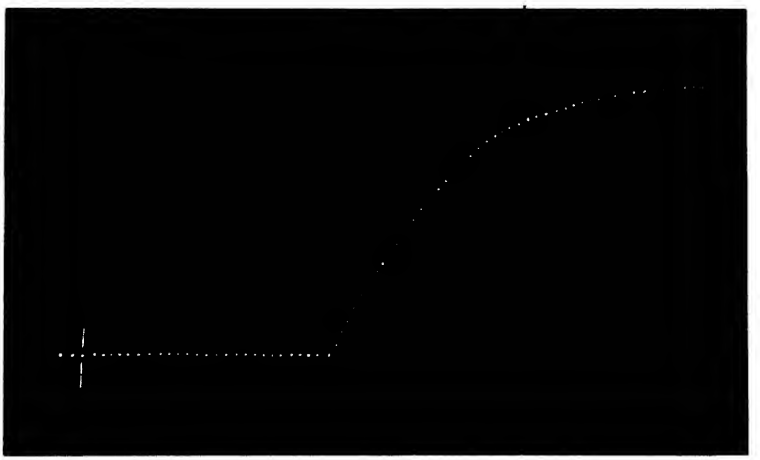

FIG. 33. Determination of Velocity of transmitted excitation in petiole of leaf when 46 days old.

The following table contains data for determination of Velocities of transmitted excitation along the petiole at different ages of the particular leaf.

TABLE X.—DETERMINATION OF VELOCITY OF TRANSMISSION OF EXCITATION AT INCREASING AGE OF THE LEAF

Specimen I

Age of leaf in days	Latent period in second	Transmission time in seconds	Velocity in mm per second
9	0·20	1·8	6·2
14	0·05	1·10	10·6
19	0·05	1·45	7·0
25	0·10	1·75	6·0
29	0·10	1·85	5·7
39	0·10	1·95	5·4
46	0·20	2·60	4·2

The following curve (fig. 34) gives a graphical representation of the relation between the Velocity of transmitted excitation and the age of the particular leaf. Inspection

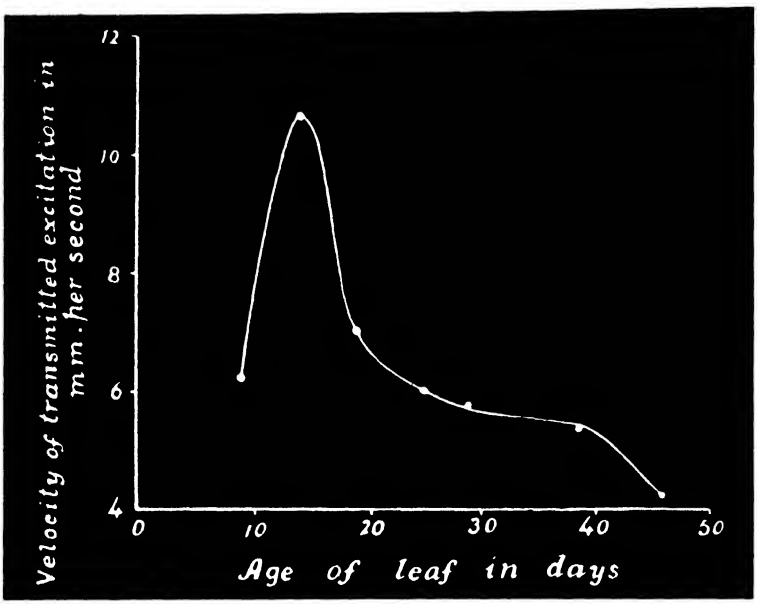

FIG. 34. Graphical representation of the relation between the Velocity of transmitted excitation in the petiole and the age of the leaf.

The ordinate represents the Velocity of transmitted excitation in mm. per second, while the abscissa indicates the age of the leaf in days.

of the curve clearly shows that the Velocity at first undergoes a rapid increase with age of the leaf; this reaches a maximum when the leaf has attained the age of 14 days. Beyond this, up to the age of 19 days, there is a marked decline in the speed of transmission. Between the ages of 20 and 39 days, further change in the Velocity is slight. But the fall in the Velocity is very marked when the leaf is 46 days old.

Confirmatory results obtained with a second specimen are given in the following table.

TABLE XI.—DETERMINATION OF VELOCITY OF TRANSMISSION OF EXCITATION AT INCREASING AGES OF THE LEAF

Specimen 2

Age of leaf in days	Latent period in second	Transmission time in seconds	Velocity in mm. per second
9	0·25	1·3	9·5
15	0·10	0·80	14·2
20	0·15	1·20	9·5
31	0·15	1·25	9·1
37	0·15	1·30	8·6
43	0·20	1·90	6·0

The general results obtained by two independent methods of inquiry on the effect of increasing age on the internal physiological activities of the plant are thus found to be of a similar character.

SUMMARY

The problem whether the internal physiological activities of organs of plant underwent any characteristic variation with the age was investigated in the case of leaf of *Mimosa pudica*.

Two independent methods were employed in this investigation for quantitative measurements of changes induced under increasing age. In the first of these, determinations were made on leaves growing on the stem which constituted age series. In the second method, the determinations were made on an identical leaf, as it grew older and older.

The changes of internal physiological activities induced by age which formed the subject of investigation were :

(1) The Amplitude of response due to contraction of the motile organ, the pulvinus.
(2) The Apex time which indicated the rapidity of contraction, as found from the determination of the period of maximum fall of the leaf.

(3) The Latent period consumed for the initiation of the responsive movement of the motile organ, the pulvinus.

(4) The Velocity of transmission of excitation in the conducting tissue of the petiole.

The results obtained with different leaves of increasing age showed that :

(1) The Amplitude of response at first increased with increasing age, the maximum activity being reached at ages between 14 and 15 days. The contractile activity exhibited progressive diminution with further advancement of age.

(2) As regards the Apex time which represents rapidity of contraction, the change induced by age is to make it progressively shorter up to the age of 13 to 15 days. Beyond this, the contractile rate exhibits relative sluggishness.

(3) The Latent period exhibits at first a progressive shortening with age, the shortest period being attained between the ages of 13 and 18 days of the leaf. Beyond this age, the Latent period exhibits increasing prolongation.

(4) The Velocity of transmission of excitation in the petiole of the leaf exhibits at first an increase of speed with the age of the leaf, the maximum value being reached between the ages of 14 and 18 days. It then undergoes a progressive diminution with the age of the leaf.

The results of determination of physiological changes induced in an identical leaf at different ages are :

(1) The Amplitude of response exhibits an enhancement with increase of age, attaining a maximum between the ages of 14 and 15 days. With further increase of age, the contractile activity exhibits a slight decline up to the age of 40 days. At still more advanced age, the contractile activity undergoes a rapid fall.

(2) The Apex time exhibits a parallel variation with the Amplitude of response.

(3) The Latent period is found at first to exhibit a

progressive shortening, the shortest period being attained between the ages of 14 and 19 days. The latter value does not undergo any marked change up to the age of 39 days. Beyond this age the Latent period becomes markedly prolonged.

(4) As regards the Velocity of transmission of excitation, it at first exhibits an increase of the rate, the maximum speed being attained between the ages of 14 and 15 days. The Velocity then undergoes a marked diminution when the age is about 20 days. The change is slight up to the age of 40 days. The Velocity, however, undergoes a rapid diminution above that age.

We take this opportunity of expressing our grateful thanks to Sir J. C. Bose for his kind suggestions and encouragement which have been extended to us throughout this investigation.

III.—THE EFFECTS OF CONTINUOUS AND OF INTERMITTENT ILLUMINATIONS ON PHOTOTROPISM

BY

S. C. DAS, M.A., AND B. K. PALIT, B.Sc.

WHEN a plant organ is subjected to unilateral photic stimulation it bends towards the light. This holds good in motile organs of not only sensitive but also of those of so-called ordinary plants. The demonstration of the latter can be made by experimenting with the pulvinule of leaflet of *Erythrina indica*. The leaf of this plant consists of the petiole *Pt*, bearing three leaflets of which two are lateral and one is terminal. The experimental devices are semi-diagrammatically represented in fig. 35. A beam of light is incident on the upper flank of the pulvinule *p* of the terminal leaflet. This latter is suitably attached by a cocoon thread *Th* to a writing lever *W*, which inscribes successive dots on a moving smoked-glass plate *G*. The dotted curve is due to the fact that the smoked-glass plate on which the record is inscribed is made to move to and fro at definite intervals by means of clockwork. In order to ensure that the record obtained represents the true responsive movement of the pulvinule only, the petiole was tied to a fixed support. The record exhibits the positive phototropic movement towards light as an up-curve.

It is obvious that the phototropic curve will be characteristically modified by the effectiveness of the light which is incident on the organ. The observed modification in the phototropic curve would then enable us to determine whether, under a definite external variation, the phototropic efficiency of the light has undergone an increase or a diminution. The phototropic curve, it should be remembered, is but one of the external manifestations of effectiveness of the incident light.

The efficiency of light can also be gauged by the rate at which the chlorophyll in the plant causes a breakdown of

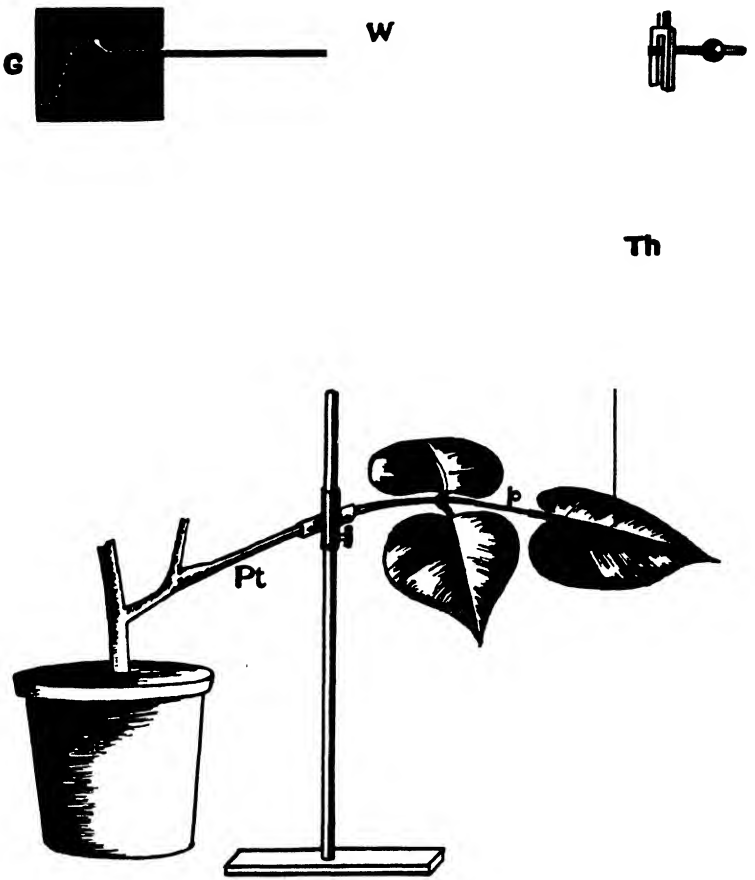

FIG. 35. Semi-diagrammatic representation of the experimental devices for record of phototropic movement of leaflet of *Erythrina indica*.

The petiole of the leaf, *Pt*, bears three leaflets, two of which are lateral and one terminal. The terminal leaflet is attached to the longer arm of the writing lever *W*, by means of a cocoon thread *Th*. Positive phototropic curvature of pulvinule *p* of the terminal leaflet is recorded on the smoked-glass plate *G* as an up-curve.

CO_2 contained in the surrounding air or water. In his work on the Physiology of Photosynthesis,[1] Sir J. C. Bose

[1] J. C. Bose, ' Physiology of Photosynthesis ' (1924), pp. 94–6.

has been able to record by an automatic method the action of light in the process of the breaking up of CO_2 with the resulting evolution of oxygen. A very remarkable result was observed by him in this connection inasmuch as intermittent illumination was found, in certain circumstances, to be more effective than continuous illumination, the actual duration of exposure being the same in the two cases. The particular circumstance which modified the efficiency was found to be the frequency of intermittence of light. Thus while quick frequency was found to be more effective than continuous light, slower frequencies became increasingly ineffective.

We undertook the present investigation to find whether there is any difference induced in phototropic reaction under continuous and intermittent lights; if this were so, we also wanted to know in what way the phototropic efficiency was modified by the frequency of intermittence of light.

In this connection it is necessary to obtain a clear idea of the fundamental reaction of light on the pulvinated organ. This reaction consists of responsive contraction of the particular flank of the organ on which light is incident. The two principal characteristics of the reaction are as follows:

1. The actual period of exposure necessary to initiate the responsive movement. This will be designated as 'Effective Period of Exposure.'
2. The Amplitude of responsive movement during exposure to light.

In determining the difference of reaction under continuous and intermittent lights of various frequencies, we shall make quantitative determinations of the characteristics mentioned above.

Experimental Method

Specimens of *Erythrina indica* grown in pots were employed for the present investigation. The potted specimen was mounted on an adjustable base by means of which the point of the writer could be brought to the desired position on the recording plate.

The experiments were carried out in a dark room between the hours of 11 A.M. and 3 P.M., during which period the

excitability of the plant was found to remain uniform. The source of light employed for stimulation was a 30 candle-power pointolite. For intermittent illumination, the pulvinule was successively exposed to equi-alternating periods of light and darkness, the durations of which were 1, 3, 5, 10 and 20 seconds. The intervals of intermission were accurately adjusted by means of rotating sectors interposed in the path of light.

Determination of 'Effective Period of Exposure'

The Effective Period of Exposure for the pulvinule was successively determined under continuous light and under intermittent exposures of varying frequencies. The curves were obtained with the Oscillating Recorder, the successive dots being inscribed on the recording plate at intervals of four seconds. The recording plate was also made to move laterally by means of clockwork at the rate of two inches per minute.

In the following series of typical experiments, the phototropic curves (*cf.* fig. 36) were obtained under continuous light and under intermittent illuminations of various frequencies.

Experiment 1. *The Effective Period of Exposure for continuous light.*—The record is shown in fig. 36, *a*. It will be seen that the phototropic movement of response was initiated at the twelfth dot; the effective period of exposure for continuous light is therefore 12×4 or 48 seconds.

The pulvinule was then allowed a resting period of 45 minutes, by which time it was found to have undergone a complete recovery. After such a recovery the organ was subjected to the action of intermittent lights of various frequencies.

Experiment 2. *Effective Period of Exposure for intermittent light of frequency of 1 second.*—The pulvinule was next subjected to intermittent light, the successive illuminations for 1 second being followed by equal duration of darkness; this will be simply described as intermittence of 1 second. The record (fig. 36, *b*) shows that the responsive movement occurred between the fourth and the fifth dot or after 18 seconds. Since the actual duration of exposure to light is for half that period, the effective period of exposure to initiate responsive movement is 9 in the place of 48 seconds

as under continuous light. Intermittent light of frequency of 1 second is therefore about 5 times more effective.

Experiment 3. *Effective Period of Exposure for inter-*

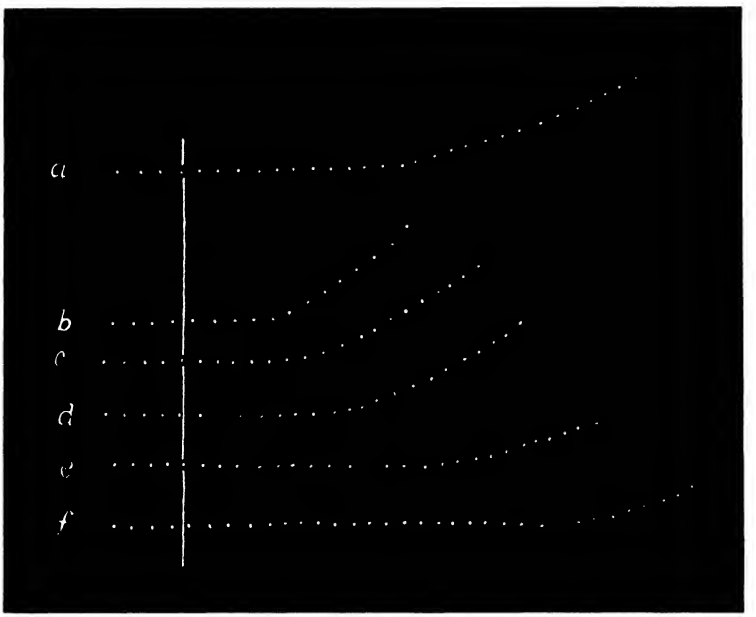

FIG. 36. Series of records demonstrating the relative effectiveness of continuous illumination and of intermittent illuminations of various frequencies.

a. The effect of continuous light; total duration of exposure for response is 48 seconds.

b. Effect of intermittent light of frequency of 1 second; total duration of exposure for response is 9 seconds.

c. Effect of intermittent light of frequency of 3 seconds; total duration of exposure for response is 12 seconds.

d. Effect of intermittent light of frequency of 5 seconds; total duration of exposure for response is 16 seconds.

e. Effect of intermittent light of frequency of 10 seconds; total duration of exposure for response is 26 seconds.

f. Effect of intermittent light of frequency of 20 seconds; total duration of exposure for response is 42 seconds.

Stimulus of light was applied at the vertical line. Successive dots in the record are at intervals of 4 seconds.

mittent light of frequency of 3 seconds. The result is seen in fig. 36, *c*. Here the effective period of exposure for inducing responsive movement was found to be 12 seconds. Though this is not as effective as under quicker frequency of inter-

mission of 1 second yet it is relatively more effective than under the action of continuous light.

Similar experiments were carried out with the same specimen under still slower intermittence. The results are demonstrated in the following series of records.

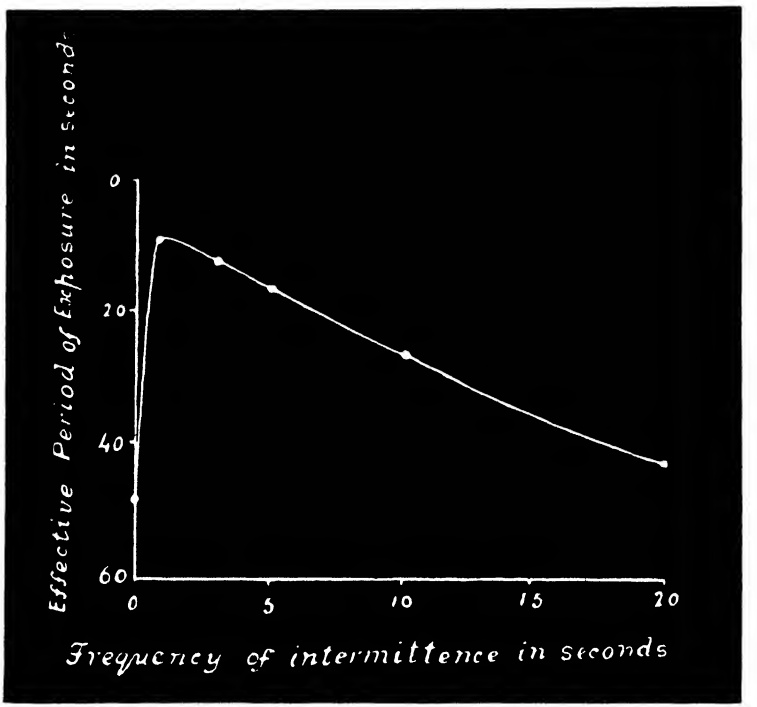

FIG. 37. Graphical representation of the variation of the Effective Period of Exposure to light under continuous and intermittent illuminations of various frequencies.
The ordinate represents the Effective Period of Exposure while the abscissa indicates the frequency of intermittence.

Under frequency of intermittence of 5 seconds (fig. 36, *d*), the total duration of effective exposure is 16 seconds.

Under frequency of intermittence of 10 seconds, the total duration of effective exposure is 26 seconds (fig. 36, *e*).

Under frequency of intermittence of 20 seconds, the duration of effective exposure had to be increased to 42 seconds (fig. 36, *f*).

In summarising the results we find that the intensity of phototropic reaction is greater with light of high frequency of intermittence than under continuous light. Further, this effectiveness under intermittent light undergoes a decline as the frequency of intermittence becomes slower. There is thus a parallelism in the relative effectiveness of continuous and of intermittent light on phototropic and photosynthetic reactions.

Returning to the question of the relative effectiveness of continuous and intermittent lights, Table I gives detailed results obtained with four different specimens, which confirm each other. Taking specimen 1 as typical, a graphical representation of the relative effectiveness of continuous and intermittent lights of various frequencies is given in fig. 37.

TABLE I.—RELATIVE EFFECTIVE PERIODS OF EXPOSURE UNDER CONTINUOUS AND INTERMITTENT LIGHTS

Specimen 1

Frequency of intermittence	The effective period of exposure
0 second	48 seconds
1 ,,	9
3 seconds	12
5 ,,	16
10 ,,	26
20 ,,	42

Specimen 2

Frequency of intermittence	The effective period of exposure
0 second	48 seconds
1 ,,	18 ,,
5 seconds	30 ,,
10 ,,	36 ,,
20 ,,	44 ,,

Specimen 3

Frequency of intermittence	The effective period of exposure
0 second	56 seconds
1 ,,	27 ,,
5 seconds	34 ,,
10 ,,	38 ,,
20 ,,	54 ,,

Specimen 4

Frequency of intermittence	The effective period of exposure
0 second	36 seconds
1 ,,	8 ,,
5 seconds	30 ,,
10 ,,	33 ,,
20 ,,	35 ,,

Amplitude of Responsive Movement during Exposure

Having determined the relative efficiencies of continuous and of intermittent illuminations as indicated by the modification of the Effective Period of Exposure, we shall next proceed to determine the Amplitude of phototropic movement induced by exposures of the same duration in cases of continuous and of intermittent illuminations of various frequencies.

The experimental arrangement is the same as that employed for the determination of the Effective Period of Exposure. The records were taken on a slower moving plate, and the interval between the successive dots in the record was adjusted to be 10 seconds. The pulvinule was first exposed to continuous illumination for a period of 1 minute and 30 seconds; it was then successively stimulated by intermittent light, the frequencies of intermission being 1, 5, 10 and 20 seconds. In order that the successive

illuminations might be of equal duration, the total length of exposure employed during intermittent illuminations had to be twice that under continuous light.

Experiment 4. *Amplitude of responsive movement under continuous light.*—The record (fig. 38, *a*) shows that under

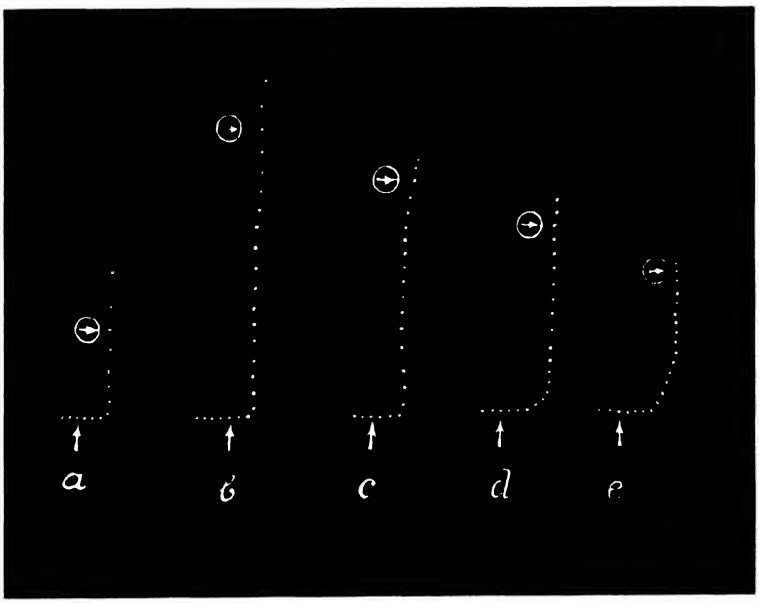

FIG. 38. Showing Amplitudes of response under continuous and intermittent lights of various frequencies.

a. The effect of continuous light.
b. Effect of intermittent light of frequency of 1 second.
c. Effect of intermittent light of frequency of 5 seconds.
d. Effect of intermittent light of frequency of 10 seconds.
e. Effect of intermittent light of frequency of 20 seconds.

The arrow in each curve at the beginning of the record indicates the moment of incidence of light and the arrow within circle its cessation. The actual duration of exposure is in all cases 90 seconds.

Successive dots are at intervals of 10 seconds.

continuous light for 1 minute and 30 seconds, the Amplitude of responsive movement was 15 mm. during the application of light.

Experiment 5. *Amplitude of response under intermittent light of frequency of 1 second.*—After allowing the usual period of 45 minutes for full recovery, the pulvinule

was subjected to intermittent light, the successive periods of illumination for 1 second being followed by an equal duration of darkness. The duration of total exposure employed in this and in the subsequent experiments was for 3 minutes, so that the actual period of exposure was the same as that under continuous light. The Amplitude of induced responsive movement is seen in this case to be very much increased, being 45 mm. or 3 times that under continuous light (fig. 38, *b*).

Experiment 6. *Amplitude of response under intermittent light of frequency of 5 seconds.*—With the frequency of intermittence of 5 seconds, the Amplitude of response is 36 mm. (fig. 38, *c*). Though this is less than that under frequency of 1 second, yet it is greater than that under continuous illumination, in which case the Amplitude was only 15 mm. (*cf.* fig. 38, *a*).

Similar experiments were carried out with the same specimen under still slower frequencies of intermittence.

With a frequency of 10 seconds, the Amplitude of responsive movement is seen to be 29 mm. (fig. 38, *d*).

In fig. 38, *e* is seen the effect of intermittence of 20 seconds. The Amplitude of response in this case is 20 mm., being less than those under the comparatively quicker frequencies of 1, 5 and 10 seconds, but greater than that under continuous light.

The results of the foregoing experiments exhibiting the relative Amplitudes of responsive movement under continuous and intermittent illuminations are embodied in the following Table.

TABLE II.—SHOWING THE AMPLITUDES OF RESPONSIVE MOVEMENT UNDER CONTINUOUS AND UNDER INTERMITTENT ILLUMINATIONS

Specimen 1

Frequency of intermittence	Amplitude of responsive movement
0 second	15·0 mm.
1 ,,	45·0 ,,
5 seconds	36·0 ,,
10 ,,	29·0 ,,
20 ,,	20·0 ,,

The following curve (fig. 39) gives a graphical representation of the variation of the Amplitude of response with the frequency of intermittence.

It will be seen from the foregoing experimental results

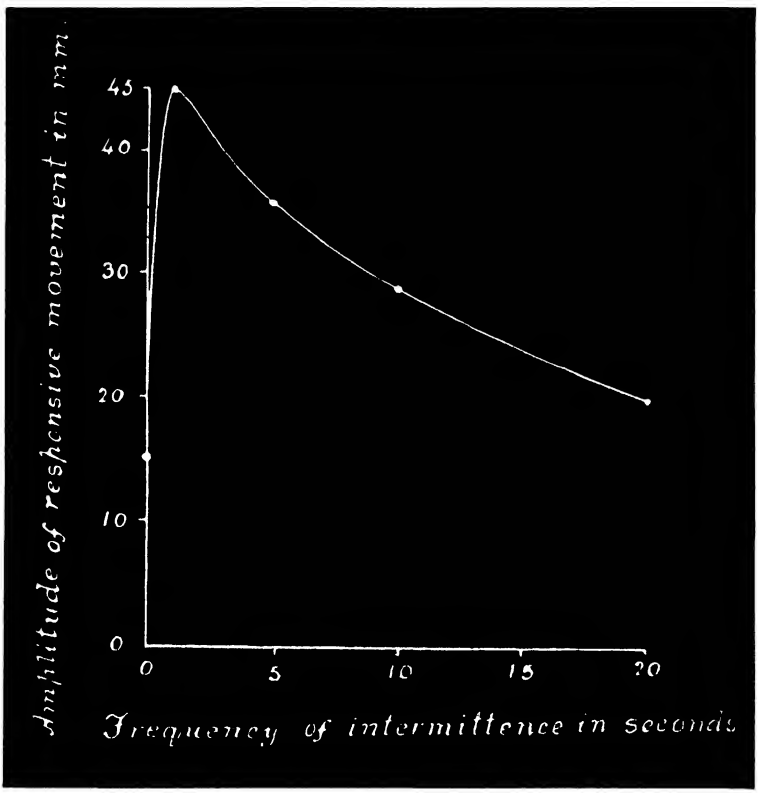

FIG. 39. Graphical representation of the variation of Amplitude of responsive movement under continuous light and intermittent illuminations of various frequencies.

The ordinate represents the Amplitude of responsive movement while the abscissa indicates the frequency of intermittence of exposure.

that the Amplitude of responsive movement increases from 15 mm. under continuous light to 45 mm. under an intermittent exposure of the quick frequency of 1 second, the increase in Amplitude being 3 times. It will further be seen that as the frequency of intermittence becomes slower, the

Amplitude of response undergoes progressive diminution. Thus while the frequency of intermittence is slowed down from 1 to 5, to 10 and finally to 20 seconds, the respective Amplitudes are reduced from 45 to 36, to 29 and lastly to 20 mm. respectively.

Confirmatory results obtained with a second specimen are given in the following table:

TABLE III.—SHOWING THE RELATIVE AMPLITUDES OF RESPONSIVE MOVEMENT UNDER CONTINUOUS AND INTERMITTENT ILLUMINATIONS

Specimen 2

Frequency of intermittence	Amplitude of responsive movement
0 second	20·0 mm.
1 ,,	50·0 ,,
5 seconds	47·5 ,,
10 ,,	37·5 ,,
20 ,,	29·5 ,,

On comparing the curves given in figs. 37 and 39, it will be evident that they closely resemble one another.

It is thus seen that whether in the modification of the Effective Period of Exposure for initiation of response or the Amplitude of responsive movement, the effectiveness of intermittent light, after attaining a maximum value at the quick frequency of 1 second, gradually decreases under still slower frequencies. In both these factors in response, moreover, intermittent illumination of frequencies between 1 and 20 seconds is seen to be more effective than continuous light.

SUMMARY

The effects of continuous and intermittent illuminations on phototropism were studied by obtaining records with the Oscillating Recorder.

Experimental investigations on the relative effectiveness of continuous and of intermittent illuminations of various frequencies were made both in regard to the Effective

Period for initiation of responsive movement and Amplitude of resulting response.

It was found that the effectiveness of intermittent light was, within certain limits, relatively greater than that of continuous light.

In regard to the two factors in response, namely, the Effective Period of Exposure and the Amplitude, they both undergo a parallel variation.

The relative efficiency of intermittent light is, moreover, found to be at its maximum at a high frequency intermittence. After this the effectiveness of intermittent light undergoes a decline as the frequency of intermittence becomes slower.

IV.—THE EFFECTS OF CONTINUOUS AND OF INTERMITTENT ILLUMINATIONS ON LONGITUDINAL GROWTH

BY

S. C. DAS, M.A., AND B. K. PALIT, B.SC.

IN our previous paper it has been shown that phototropic reaction becomes more effective under intermittent illumination of quick frequency than under continuous light. Moreover this effectiveness, within limits, is greater under quicker frequencies of intermittence than under slower ones. Reference was also made to the fact demonstrated by Sir J. C. Bose in his work on Photosynthesis.[1] that parallel reactions are met with in the carbon assimilation of plants under continuous and intermittent lights.

Since phototropic movement is brought about by differential growth induced at the proximal and distal sides of the organ by the action of unilateral light, we next undertook investigations on the action of continuous and of intermittent lights in modification of growth itself. This was carried out by obtaining records of longitudinal growth of the organ when acted upon on all sides by continuous and by intermittent lights of various frequencies.

EXPERIMENTAL ARRANGEMENT

The determination of growth elongation was made with the High Magnification Crescograph,[2] which consisted of a compound system of two levers. The specimen was attached to the first lever at a short distance from the fulcrum; the second or the recording lever suitably attached to the first produced a further magnification. The total compound magnification produced for the record was

[1] J. C. Bose, 'Physiology of Photosynthesis' (1924), pp. 94–6.
[2] J. C. Bose, 'Growth and Tropic Movements of Plants,' p. 8.

2,500 times. The recording plate was kept oscillating at intervals of 30 seconds, so that the distance between the successive dots gave measurements of magnified longitudinal growth during that interval. Records were taken on a stationary plate. Enhancement of growth caused wider spacings between the successive dots. Diminution of the rate was, on the other hand, shown by the closeness of the dots.

For the study of the effects of photic stimulation on growth the source of illumination employed was a 100 candle-power pointolite. For absorbing the heat rays the beam of slightly convergent light was first allowed to traverse a rectangular water trough made of parallel faces of glass, the intervening breadth of water column being one inch. The beam of light after emerging from the water trough was made to act on the specimen, which was placed between two suitably inclined mirrors so that light acted simultaneously on all sides of the organ. Experiments were performed in a dark room between the hours of 10 A.M. and 4 P.M., during which period the temperature of the room remained practically constant at or near 28·5° C.

The specimen employed for the investigation was *Cosmos*. Selected seedlings about 3 to 4 inches in height were transferred from the plant bed to small earthen pots, the top of the earth being covered over with moist blotting-paper. The potted plant was mounted on a base provided with a fine rack and pinion arrangement, with the help of which the point of the writing lever could be brought to the desired position on the recording plate. The basal end of the plant was clamped to a fixed support. The tip of the plant, just below the bunch of leaves, was then attached by means of glass links of suitable lengths to the first lever at a short distance from the fulcrum.

The rate of growth in darkness was first recorded. The plant was then successively stimulated by continuous light and by intermittent illuminations in which the intervals of intermission were gradually increased. The intermittent exposures consisted of equi-alternating periods of light and darkness, the different periods being 1, 5, 10 and 20 seconds. The normal growth rate in darkness was observed at the beginning of each series of exposures to light, in order to be certain that the plant had undergone complete recovery from the preceding stimulation. A complete recovery was

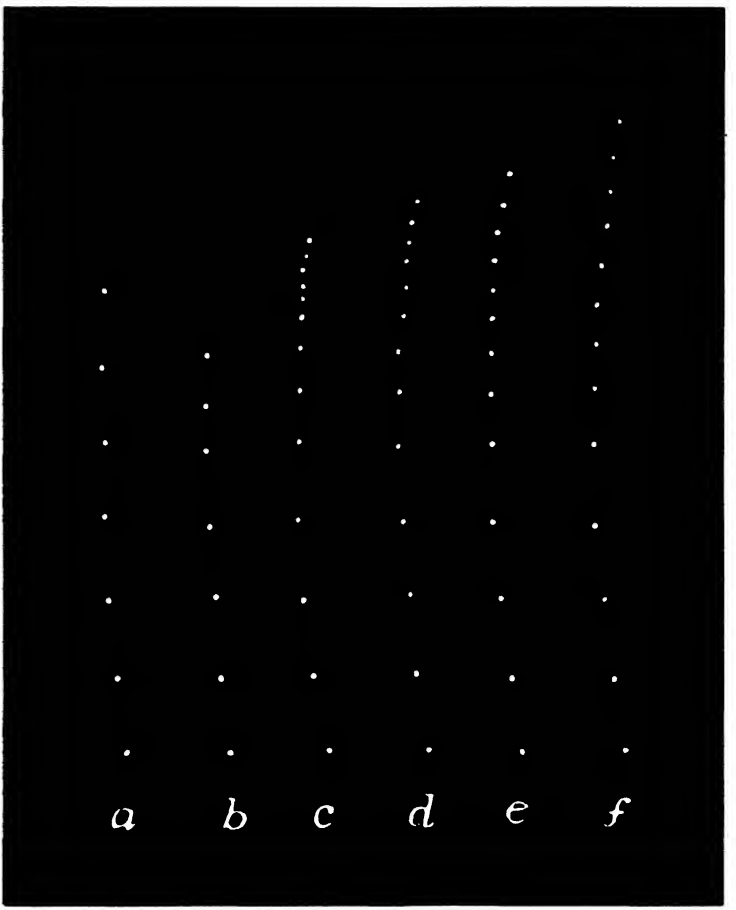

FIG. 40. Series of records exhibiting the effects of continuous light and of intermittent illuminations of different frequencies in inducing modification of growth.

a. Record of growth in darkness.
b. Effect of continuous light of 3 minutes duration.
c. Effect of intermittent light, frequency of intermission being 1 second.
d. Effect of intermittent light, frequency of intermission being 5 seconds.
e. Effect of intermittent light, frequency of intermission being 10 seconds.
f. Effect of intermittent light, frequency of intermission being 20 seconds.

Successive dots are at intervals of 30 seconds.

found to have been effected after a period of rest of 45 minutes.

It should be borne in mind that there is a pulsatory variation in growth which exhibits itself when its record is taken at short intervals. But the *average rate* of normal growth for a fair length of time may be regarded as constant.

Determination of Rate of Growth under Darkness

Experiment 1.—The first line in the record (fig. 40, *a*) shows the longitudinal growth in darkness, the intervening spaces between successive dots representing the magnified longitudinal growth in the course of 30 seconds; the entire length of the record represents the longitudinal growth for a period of 3 minutes. The magnified longitudinal growth for 3 minutes is thus found to be 60 mm. The average rate of growth g in μ per second is calculated from the formula :

$$g = \frac{G}{m \times t} \times 10^3 \ \mu \text{ per second}$$

where g = rate of growth in μ per second.
G = magnified longitudinal growth in mm.
m = magnification (2,500 times).
t = time in seconds.

The rate of growth in darkness is therefore :

$$\frac{60}{2500 \times 3 \times 60} \times 10^3 \ \mu, \text{ or } 0{\cdot}133 \ \mu \text{ per second.}$$

Determination of Rate of Growth under Continuous Light

Experiment 2.—The second line in the record (fig. 40, *b*) shows the retardation induced in growth under continuous light. The specimen was exposed to light, the record being commenced at the lowermost point of the curve. The duration of application of light was for 3 minutes. The record indicates that while the average rate of growth under continuous light during the first minute was 0·133 μ, it was reduced to 0·125 μ during the second minute, while during the third minute it was further retarded to 0·083 μ. This proves that the rate of growth under continuous illumination undergoes increasing retardation with the duration of exposure (*cf.* Table I, A).

DETERMINATION OF RATE OF GROWTH UNDER INTERMITTENT ILLUMINATION

In the following series of experiments the effects of intermittent lights of various frequencies were studied. Since the exposure was intermittent, exposure to light being followed by an equal period of darkness, the total duration of the experiment had to be 6 minutes, so that the actual exposure was the same in all cases, namely 3 minutes.

Experiment 3. *Determination of rate of growth under intermittent light of frequency of* 1 *second.*—The third line in the record (fig. 40, *c*) shows the effect of intermittent light, the duration of successive intermissions being 1 second. It is thus found that while actual exposure of 1 minute to intermittent light of frequency of 1 second induced a negligible retardation (normal rate being 0·133 μ), after 2 minutes exposure the rate was reduced to 0·041 μ. After 3 minutes actual exposure it had further declined to 0·025 μ per second. It is thus seen that while under continuous light the rate of growth had become retarded in the course of 3 minutes exposure, from the normal 0·133 μ to 0·083 μ, under intermittent light of frequency of 1 second it had undergone a very much greater retardation, the rate being reduced to 0·025 μ per second.

Experiment 4. *Determination of the rate of growth under intermittent light of frequency of* 5 *seconds.*—The effect of intermittent light of frequency of 5 seconds is seen in the record (fig. 40, *d*). Here also it is found that under intermittent light the decline in the rate of growth is greater than that under continuous light. For while in the latter case the retarded rate of growth is 0·083 μ, in the present case it is 0·036 μ per second. The retardation in the rate of growth is not, however, so great as under the quicker frequency of intermission of 1 second, in which case it was 0·025 μ per second.

Experiment 5. *Determination of the rate of growth under intermittent light of frequency of* 10 *seconds.*—In fig. 40, *e* is seen the modification of growth under intermittent light of frequency of 10 seconds. The retarded rate of growth is seen to be 0·050 μ per second after 3 minutes actual exposure (*cf.* Table I, D). The decline in the rate of growth, though greater than that under continuous light, is, however, less

than that under the relatively quicker frequencies of 1 and 5 seconds (*cf.* Experiments 3 and 4).

Experiment 6. *Determination of the rate of growth under intermittent light of frequency of 20 seconds.*—In the last line of the series (fig. 40,*f*) is seen the effect of intermittent light of the comparatively slower frequency of 20 seconds. The retarded rate of growth is seen to be 0·070 μ per second (*cf.* Table I, E). The retardation in the rate of growth is also found here to be greater than that under continuous light but less so than under the comparatively quicker frequencies of 1, 5 and 10 seconds.

It is thus found that while the normal rate of growth of 0·133 μ per second was lowered to 0·083 μ during exposure under continuous light, the retarded growth rates under intermittent illuminations of frequencies 1, 5, 10 and 20 seconds were 0·025 μ, 0·036 μ, 0·050 μ and 0·070 μ respectively.

A tabular statement of the results is given below.

TABLE I.—SHOWING THE RATES OF GROWTH AT SUCCESSIVE MINUTES OF ACTUAL EXPOSURE TO CONTINUOUS AND INTERMITTENT LIGHTS

(Normal rate of growth 0·133 μ per second)

A. *Effect of Continuous Light*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute	20·00	0·133 μ
Second minute	18·75	0·125 μ
Third minute	12·50	0·083 μ

B. *Effect of intermittent light; frequency 1 second*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute	20·00	0·133 μ
Second minute	6·25	0·041 μ
Third minute	3·75	0·025 μ

C. *Effect of intermittent light; frequency* 5 *seconds*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	20·00	0·133 μ
Second minute . .	7·50	0·050 μ
Third minute . .	5·50	0·036 μ

D. *Effect of intermittent light; frequency* 10 *seconds.*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	20·00	0·133 μ
Second minute . .	7·50	0·050 μ
Third minute . .	7·50	0·050 μ

E. *Effect of intermittent light; frequency* 20 *seconds.*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	20·00	0·133 μ
Second minute . .	11·50	0·076 μ
Third minute . .	10·50	0·070 μ

The following curve (fig. 41) gives a graphical representation of the retardation in the rate of growth under continuous light and under intermittent lights of various frequencies, from data supplied by Table I.

The curve (fig. 41) clearly indicates that intermittent light is even more effective in retardation of growth than continuous light. Further, this effectiveness is at its maximum when the frequency of intermittence is at its quickest, becoming relatively less effective with the slowing down of the frequency of intermission.

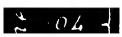

FIG. 41. Graphical representation of the retardation in the rate of growth under continuous light and intermittent illuminations of various frequencies.
The ordinate represents the rate of growth while the abscissa indicates the frequency of intermittence of exposure.

Experiments carried out with two other specimens (see Tables II and III) gave results which confirm those already given.

TABLE II.—SHOWING THE RATES OF GROWTH AT SUCCESSIVE MINUTES OF ACTUAL EXPOSURE TO CONTINUOUS AND INTERMITTENT LIGHTS

(Second Specimen : Normal rate of growth 0·160 μ per second)

A. *Effect of continuous light*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	20·00	0·133 μ
Second minute . .	18·50	0·123 μ
Third minute . .	16·00	0·106 μ

B. *Effect of intermittent light; frequency* 1 *second*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	16·00	0·106 μ
Second minute . .	6·40	0·042 μ
Third minute . .	6·40	0·042 μ

C. *Effect of intermittent light; frequency* 5 *seconds*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	17·60	0·117 μ
Second minute . .	8·00	0·053 μ
Third minute . .	8·00	0·053 μ

D. *Effect of intermittent light; frequency* 10 *seconds*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	19·20	0·128 μ
Second minute . .	9·50	0·063 μ
Third minute . .	9·50	0·063 μ

E. *Effect of intermittent light; frequency* 20 *seconds*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	19·20	0·128 μ
Second minute . .	15·00	0·100 μ
Third minute . .	14·20	0·094 μ

TABLE III.—SHOWING THE RATES OF GROWTH AT SUCCESSIVE MINUTES OF ACTUAL EXPOSURE TO CONTINUOUS AND INTERMITTENT LIGHTS

(Third Specimen : Normal rate of growth 0·160 μ per second)

A. *Effect of continuous light*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of gro per secon
First minute . .	21·00	0·140 μ
Second minute .	11·20	0·074 μ
Third minute . .	9·50	0·063 μ

B. *Effect of intermittent light ; frequency* 1 *second*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	11·00	0·073 μ
Second minute .	6·70	0·044 μ
Third minute . .	3·75	0·025 μ

C. *Effect of intermittent light ; frequency* 5 *seconds*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	18·75	0·125 μ
Second minute .	8·75	0·058 μ
Third minute . .	5·60	0·037 μ

D. *Effect of intermittent light ; frequency* 10 *seconds*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	18·75	0·125 μ
Second minute .	8·75	0·058 μ
Third minute . .	6·80	0·045 μ

E. *Effect of intermittent light; frequency 20 seconds*

Duration of actual exposure	Longitudinal growth in mm. per minute	Rate of growth per second
First minute . .	18·75	0·125 μ
Second minute .	9·50	0·063 μ
Third minute . .	7·50	0·050 μ

The results obtained with the second and third specimens also prove that the effectiveness of light, in inducing retardation of rate of growth, is maximum under the relatively quicker frequency of 1 second. Further, with the slowing down of the frequency of intermission, the effectiveness undergoes a progressive diminution.

Summary

The effects of continuous and intermittent lights in retardation of longitudinal growth were investigated by means of the High Magnification Crescograph and special devices for producing intermittent lights of various frequencies.

It was found that the retardation induced in the rate of longitudinal growth is, generally speaking, greater under intermittent illuminations than under continuous light.

In regard to the retardation of growth induced by intermittent lights of various frequencies, the action of quick frequency of intermission is found to be relatively more effective than those induced by slower frequencies.

A wider generalisation is reached in regard to the action of continuous and interrupted lights on green plants. All diverse activities in these plants such as photosynthesis, phototropism and the activity of growth are found to undergo modifications which are essentially of a similar character.

We take this opportunity of expressing our grateful thanks to Sir J. C. Bose for his kind suggestions and encouragement which have been extended to us throughout this investigation.

V.—INVESTIGATION ON THE 'AFTER-RIPENING' OF THE SEED

BY

B. K. DUTT, B.Sc., AND A. GUHA THAKURTA

MOST of the seeds, after full maturation, are not capable of germination immediately after harvest; a few weeks or months later they are, however, able to germinate quickly and uniformly. This phenomenon of dormancy has been termed 'After-ripening.' This dormant period has been observed by different investigators to vary in different kinds of seeds from a few weeks to over a year. After-ripening dormancy is, however, absent in a few viviparous seeds, in which there is no resting stage in the development of the seed, from the fertilization of the egg-cell to the production of seedlings with well-developed leaves.

In the non-viviparous seeds, after fertilization of the egg-cell the zygote gradually develops into a miniature plant, but at a certain stage of its development further progress is held in abeyance until germination. The period of this dormancy of the seed is known as the *After-ripening* or the *Resting stage.* The whole period prior to this condition may conveniently be termed the *Pre-resting stage.* The seed which has passed over the period of dormancy may be said to have attained the *Post-resting stage.* In exploring the cause of the resting stage of the embryo divergent conclusions have been arrived at by different investigators; some have attributed it to the embryo itself, others to the properties of other developing structures.

The object of the present paper is for investigation of the factors associated with the after-ripening dormancy in the seed of a particular variety of *Cajanus.* It was ascertained from a preliminary examination that (*a*) the green seeds of *Cajanus* freshly harvested from the plant are capable of immediate germination and (*b*) the seeds harvested

after the attainment of dry stage fail to do so. This led us to believe that the after-ripening dormancy is probably attained in the seed at a particular stage of maturity and that before this stage has been reached it is capable of germination. For testing the soundness of this conclusion, investigations were carried out in the following directions :—

(1) Determination of the exact stage of maturity of seed for attainment of after-ripening dormancy.

(2) Determination of the factors associated with the dormancy of the seed at the after-ripening stage.

Some additional observations were also made on the influence of moisture content of the resting seed of *Cajanus* in the period of after-ripening.

Determination of the Exact Stage of Maturity for the After-ripening Dormancy

The moisture percentage of the seed is progressively lowered as it advances towards the stage of maturity. This condition universally occurs in all seeds. Hence the moisture percentage we regarded as a criterion for the determination of maturity. For the determination of the exact moisture condition at which the dormancy may be said to be initiated, the capability of germination and moisture content were observed side by side at different stages, from the green immature to the brown dry states of the seed.

Pods of different ages were collected from the plant. Seeds were carefully separated from the pods and those similar in maturity were grouped together. In this way a number of groups were obtained in each harvest.

The great difficulty in the selection was that in regard to their size and colour, seeds of the same age and even of the same pod sometimes varied considerably from one another, their respective moisture content and maturity being therefore very different. Again, the apparent difference amongst the individual members of the same pod was in certain cases not very striking. There was, however, no other alternative but eye-observation in making different groupings of the seeds. Those which appeared to be alike in colour and size were therefore grouped together. Personal error is liable to enter in this method of grouping, the error being to a considerable extent averted after practice. The

proportion of error was independently judged from the time of germination of the individual members of each group.

After making a number of such groupings ten seeds were taken from each group. These samples were separately soaked in water. The dishes in which the seeds were soaked were numbered in accordance with the group to which the seeds belonged. The time of germination which was indicated by the time of extrusion of the radicle was recorded in each case in each group. In order to determine whether plants could be raised from the germinated seeds they were kept under observation till the formation of well-developed seedlings.

The moisture percentage of each of the above groups was decided by dehydration of a quantity of seeds which corresponded to each of the above. The dehydration was produced by placing the seeds for a period of six hours in a steam oven maintained at 100° C.; the total moisture of the seeds was found to be eliminated even in the shorter period of five hours.

The results of the experiments in which the times of germination were noted are given in tabular form. The data have been arranged in the descending order of moisture percentage. For the sake of convenience of inspection they have been embodied in four tables. Table I shows all the results of experiments having the moisture percentage between 80 and 50; while those between 50 and 30, 30 and 15, and 15 and 5 have been embodied in Tables II, III, and IV respectively.

It is seen in Table I that at 80·1 per cent. moisture content of the seed there is no germination. Similar is the case with 65·2, 60·1, and 59·7 per cent. moisture content. At 59·1 per cent., 1 germinated after 120 hours. At 58·1 per cent. 3 germinated after 140 hours. At 56·3 per cent. all the seeds or cent. per cent. germinated after 120 hours. From 56·3 per cent. downwards to 50·1 per cent. the time required for germination is seen to be progressively decreased.

From the results of the experiments detailed in the tables, it would appear that the resting stage occurs in the seed of *Cajanus* when its moisture percentage is as low as about 10 per cent. In the pre-resting condition, seeds are, however, capable of germination even when the moisture percentage is as high as 58; above this percentage the power of germination remains undeveloped.

TABLE I.—GERMINATION TIME OF THE SEEDS OF *CAJANUS* HAVING THE MOISTURE CONTENT BETWEEN 80 AND 50 PER CENT.

(Total number of seeds taken from each group, 10)

Moisture content of the seeds	Number of seeds germinated at the end of number of hours																	
	76	80	84	88	92	96	100	104	108	112	116	120	124	128	132	136	140	144
80·1																		
65·2																		
60·1																		
59·7																		
59·1												1						
58·1																	3	
56·3												10						
56·2												6				3		
55·6											8		2					
51·1			6	4														
50·1	9					1												

TABLE II.—GERMINATION OF THE SEEDS OF *CAJANUS* HAVING THE MOISTURE CONTENT BETWEEN 50 AND 30 PER CENT.

(Total number of seeds taken from each group, 10)

Moisture percentage of the seeds	Number of seeds germinated after designated number of hours								
	16	18	20	22	24	26	28	30	32
47·2							8	2	
46·1						9	1		
45·2					7	3			
42·2			7		3				
40·6		10							
40·5		9		1					
39·1	3	7							
38·9	10								
37·3	6	4							
36·2	2	8							
35·1		10							
34·2		6	4						
32·3		3	7						
30·6			7	2	1				
30·5			10						

From inspection of the different tables it would further appear that the moisture percentage of the pre-resting seed has a very important bearing on the time taken for germination. Thus the time of germination varies from 16 to

TABLE III.—GERMINATION OF THE SEEDS OF *CAJANUS* HAVING THE MOISTURE CONTENT BETWEEN 30 AND 15 PER CENT.

(Total number of seeds taken from each group, 10)

Moisture percentage of the seeds	Number of seeds germinated after designated number of hours														
	24	28	32	36	40	44	48	52	56	60	64	68	72	76	80
28·06	8	2													
26·13	2	8													
24·31		9	1												
23·03			10												
22·5		9		1											
22·32			7	3											
20·35				6	4										
19·06				10											
18·82					10										
16·2							7	2					1		
15·9													6	4	
15·2													4	4	2
15·13											8	2			

18 hours in the seeds having the moisture content between 36 and 40 per cent., which may be regarded as the optimum condition of moisture for germination; this minimum period gradually increases as the moisture condition for

TABLE IV.—GERMINATION OF THE SEEDS OF *CAJANUS* HAVING THE MOISTURE CONTENT BETWEEN 15 AND 5 PER CENT.

(Total number of seeds taken from each group, 10)

Moisture percentage of the seeds	Number of seeds germinated after designated number of hours																
	76	80	84	88	92	96	100	104	108	112	116	120	124	128	132	136	140
14·6	10																
14·1	7	3															
14·0	7	3															
13·8				9													
12·3																	2
10·2												1					
9·2																	
8·21																	
8·2																	
6·9																	
6·32																	
5·33																	
5·02																	

germination is increased or decreased above or below the optimum.

From the data given in the tables, the relation of moisture content of the pre-resting seed with the time of germination

FIG. 42. Graphic representation of the relation between moisture content and time of germination of the seed of *Cajanus indica* in the pre-resting condition.

is graphically represented in fig. 42. As all the seeds of the same group did not germinate exactly at the same time, the nearest time in which at least 60 per cent. of the seeds germinated has been computed as the average time of germination for the particular group.

In the seeds of low moisture content we made the interesting observation that the time of germination greatly depended on the absorption of water. The seeds with low moisture content were found slow in absorbing water; but when they had become fully swollen they germinated unfailingly within 12 to 20 hours.

Determination of Certain Factors associated with Dormancy of the Seed at the After-Ripening Stage

From the results of the before-mentioned experiments it may be concluded:

(1) That the resting stage in *Cajanus* occurs when its moisture content is as low as about 10 per cent.

(2) That during the resting stage the seeds are incapable of absorbing moisture. Such seeds when kept in water even for such a long period as a month, did not absorb water.

The most important condition for germination of the seed is, therefore, its capacity for absorption of water. The embryo of the post-resting seed cannot germinate unless the seed becomes swollen by absorption of sufficient quantity of water. This inference may be tested by the following experiments.

(1) Is it the difficulty of absorption of water across the seed-coat that obstructs the germination? In that case the removal of the seed-coat should bring about quick germination. This was found to be actually the case, for all the seeds from which the seed-coat was removed became swollen within a short time, with resulting germination and production of normal seedlings.

(2) Without having recourse to the drastic step of total removal of the seed-coat of the resting seed, a single pin prick was made on it. The experiment was carried out with nine different specimens all having low moisture content. The size of the pin prick was made similar in all cases. In Table V are given details of results obtained.

TABLE V.—GERMINATION OF THE SEED OF *CAJANUS* AT THE AFTER-RIPENING STAGE AFTER PIN-PRICK

No. of Exp.	Moisture content	Number of seeds	Time of complete swelling	Time of germination	Percentage germination
	%		hrs.		
1.	5·02	10	9	8 after 24 hrs. 2 ,, 28 ,,	100
2.	8·5	10	5	10 ,, 20 ,,	100
3.	9·2	10	5	10 ,, 20 ,,	100
4.	6·5	10	7	4 ,, 20 ,, 6 ,, 24 ,,	100
5.	7·61	10	6	6 ,, 20 ,, 3 ,, 22 ,, 1 ,, 28 ,,	100
6.	6·5	10	7	9 ,, 24 ,, 1 ,, 28 ,,	100
7.	5·82	10	8	7 ,, 24 ,, 2 ,, 28 ,, 1 ,, 36 ,,	100
8.	8·15	10	5	10 ,, 20 ,,	100
9.	9·25	10	5	4 ,, 18 ,, 6 ,, 20 ,,	100

The results summarised in the above table appear to show that resting seeds with lower moisture content require longer time to swell; moreover, the delayed germination in those seeds appears to be related to the time required for swelling. After the complete attainment of swelling the time required for germination was almost equal in all the seeds though of different moisture content.

FIG. 43. Photo-micrograph of a section of the seed-coat of *Cajanus* showing the injury on the outermost region of the testa due to a slight scratch (magnified 170 times).
A, place of injury; B, testa and tegmen fused together; C, perisperm.

The results of the above experiments also make it clear that it is the outer structure alone which is concerned with the after-ripening dormancy of the seed of *Cajanus* and that it is the development of some condition in the outer structure that prevents the absorption of water.

The next point of our inquiry related to the determination of the particular region of the outer structure to which this condition is due; could this be the seed-coat or the hilum? This was determined by completely sealing up the hilum

in the pre-resting and post-resting conditions; the seeds after sealing of the hilum were still found readily to absorb water. Moreover, the times taken for swelling of the sealed and unsealed seeds were found to be practically the same. It would thus appear that the hilum plays a very insignificant part, if any at all, in the absorption of water and that the absorption of water occurs mainly, if not wholly, across the seed-coat. It is thus quite reasonable to come to the conclusion that in the resting stage some condition is produced in the seed-coat which prevents the absorption of water.

The next problem to be solved is as to whether this impermeability is developed throughout the whole thickness of the seed-coat. For arriving at a decision on the subject a slight scratch was made on the upper surface of the seed-coat by a piece of fine sandpaper. The result of this was that the resting seed became swollen in water. When a transverse section was made across the scratch and examined under a microscope (see fig. 43), it was found that the injury occurred only on the outermost layer of the testa. It is therefore natural to conclude that in the resting stage it is the development of some condition in the outermost layer of the testa that makes the seed impervious to water.

Influence of Moisture Content of the Resting Seed of *Cajanus* on the Period of After-Ripening

It has been shown previously (*cf.* Table IV) that the after-ripening stage commences in the seed of *Cajanus* when its moisture content falls down to the neighbourhood of 10 per cent. The seed can now be stored at this or at a still lower percentage of moisture content, which results from the further drying of the seed after the attainment of the resting stage.

It is the general agricultural practice to dry the seeds perfectly before storing; the capacity for germination of the seed has been found to be prolonged under this particular condition.

In our next experiment, we made attempts to find out whether the percentage of moisture of the resting seed has any influence on the length of the after-ripening period. In order to note the exact time of after-ripening, seeds were collected from moderately dry pods. The seeds of fully

dried pods in which the resting stage had already been attained were discarded, since in these the resting stage had already been attained at an undefined earlier period. The partially dried seeds were then carefully separated from the pods, so that the coats received no injury. In selecting the seeds uniformity of size, shape and colour was taken into account, and seeds that appeared to be of equal maturity were selected for observation. The moisture content of the collected seeds was determined by dehydrating a quantity of the sample. Thereafter the seeds were dried in the sun for rapid evaporation of moisture. After drying for a day or two, when the moisture content of the seed had fallen below 10 per cent. they were stored in a stoppered glass jar. A quantity of the seed, ten in number, was placed in water to make certain that there was no swelling by absorption of water, which gave indication that the after-ripening condition had been attained by the seed. Different batches of ten similar seeds were placed in water at definite intervals after storage so as to find out when the resting stage was passed, as indicated by appearance of germination. The results of a few typical experiments with seeds having different moisture contents are given in the following Tables (VI, VII, VIII, IX).

In order to make the meaning clear, we shall refer in some detail to the results given in Table VI. The seeds were collected on February 28, 1935, the moisture content being 9·2 per cent. The successive dates at which the seeds were soaked in water are given in the third column, and the results given in the fourth. There is no germination of seeds soaked in water up to April 12, 1935. After that date the soaked seeds began to germinate with increasing effectiveness. The conclusion arrived at is that the resting period of the particular group extended up to April 25, 1935, or 55 days. The effect of less moisture content of 8·51 per cent. is shown in Table VII. Here the resting period is lengthened to 72 days.

The results of various experiments show that the after-ripening period of the seed is longer when the moisture percentage is low, while it is shorter when the moisture percentage is high.

TABLE VI.—INDICATING THE TOTAL PERIOD OF AFTER-RIPENING OF THE SEED OF *CAJANUS*

(Moisture content 9·2 per cent.)

Date of collection	Moisture content when stored	Dates of soaking	Number germinated as result of swelling out of batches of 10
	%		
28/2/35	9·2	1/3/35	nil
		18/3/35	nil
		1/4/35	nil
		12/4/35	nil
		25/4/35	2 germinated after 192 hrs. the rest did not
		15/6/35	5 germinated after 24 hrs. 3 ,, ,, 72 hrs. 1 ,, ,, 96 ,, 1 ,, ,, 168 ,,
		2/7/35	5 germinated after 24 hrs 2 ,, ,, 48 ,, 2 ,, ,, 72 ,, 1 did not
		15/7/35	4 germinated after 24 hrs. 4 ,, ,, 48 ,, 1 ,, ,, 72 ,, 1 ,, ,, 96 ,,

TABLE VII.—INDICATING THE TOTAL PERIOD OF AF
OF THE SEED OF *CAJANUS*

(Moisture content 8·51 per cent.)

ıte of ection	Moisture content when stored	Dates of soaking	Number germinated i swelling out of batcl
1/35	% 8·51	2/1/35	nil
		17/1/35	nil
		2/2/35	nil
		18/2/35	nil
		1/3/35	nil
		15/3/35	1 germinated after 120 hrs. the rest did not
		1/4/35	1 germinated after 72 hrs. 2 ,, ,, 120 ,, the rest did not
		16/4/35	2 germinated after 96 hrs. 2 ,, ,, 120 ,, 1 ,, ,, 168 ,, the rest did not

.—INDICATING THE TOTAL PERIOD OF AFTER-RIPENING OF THE SEED OF *CAJANUS*

(Moisture content 8·21 per cent.)

Moisture content when stored	Dates of soaking	Number germinated as result of swelling out of batches of 10
% 8·21	4/2/35	nil
	23/2/35	nil
	13/3/35	nil
	28/3/35	nil
	11/4/35	nil
	25/4/35	2 germinated after 144 hrs. the rest did not
	15/6/35	3 germinated after 24 hrs. 4 ,, ,, 96 ,, the rest did not
	2/7/35	4 germinated after 24 hrs. 3 ,, ,, 72 ,, 1 ,, ,, 96 ,, the rest did not
	15/7/35	4 germinated after 24 hrs. 2 ,, ,, 48 ,, 2 ,, ,, 96 ,, the rest did not

TABLE IX.—INDICATING THE TOTAL PERIOD OF AFTER-RIPENING OF THE SEED OF *CAJANUS*

(Moisture content 5·33 per cent.)

Date of collection	Moisture content when stored	Dates of soaking	Number germinated as result of swelling out of batches of 10
	%		
1/1/35	5·33	6/1/35	nil
		21/1/35	nil
		6/2/35	nil
		21/2/35	nil
		6/3/35	nil
		21/3/35	nil
		6/4/35	nil
		21/4/35	2 germinated after 96 hrs. 1 ,, ,, 240 ,, the rest did not
		15/6/35	2 germinated after 20 hrs. 3 ,, ,, 76 ,, 2 ,, ,, 120 ,, 1 ,, ,, 168 ,, the rest did not.
		2/7/35	3 germinated after 20 hrs. 3 ,, ,, 48 ,, 2 ,, ,, 120 ,, the rest did not
		15/7/35	3 germinated after 20 hrs. 2 ,, ,, 48 ,, 3 ,, ,, 72 ,, 1 ,, ,, 140 ,, the rest did not

Summary

The experiments carried out with the seeds of a particular variety of *Cajanus* show that the after-ripening dormancy is reached when the moisture content is as low as 10 per cent. The pre-resting seeds are capable of germination when the moisture content is as high as 56 per cent.; but with still higher percentage of moisture, the capacity for germination is found to be undeveloped.

Pre-resting seed with a moisture content of 36 to 40 per cent. germinates within 16 to 18 hours, this being the shortest time required for germination of the seed in the pre-resting condition.

The time taken for germination gradually increases as the moisture content increases above or decreases below that in the optimum condition.

The resting seed is capable of immediate germination by absorption of water when the seed-coat is either removed or pricked with a pin.

It is also found that the time of germination which results from swelling, by absorption of water, is greater the lower the water content of the seed in the resting stage. After swelling, the actual time taken for germination is almost the same in all the seeds though they may have different moisture contents.

The seed is permeable to water in the *pre-* and *post-*resting stages. In the resting stage, however, some condition in the coat prevents the absorption of water. The factor which confers impermeability is not extended throughout the whole thickness of the seed-coat; it is most effectively present in the outermost layer of the testa.

The percentage of moisture of the resting seed has an important bearing on the length of the after-ripening period; the period is considerably lengthened when the percentage of moisture is low.

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VI.—EFFECT OF VARIATION OF TEMPERATURE ON THE RESPIRATION OF FLOWER (*HELIANTHUS ANNUUS*)

BY

A. GUHA THAKURTA AND B. K. DUTT, B.Sc.

THE study of the effect of temperature on the respiration of plants has been undertaken in different directions by a large number of investigators; but the conclusions arrived at by them on the relation between temperature and respiration are not wholly concordant. An attempt is made in the present paper to re-investigate some of the problems by means of a more accurate and sensitive device and thereby to determine more fully the effects of temperature on respiratory activity of the plant.

The investigations undertaken were:

(1) On the Effect of Increase of Temperature on Respiration.
(2) On the Determination of Temperature Coefficient of Respiration.
(3) On the Determination of the Optimum Temperature.
(4) On the Effect of Decrease of Temperature on Respiration.

Moderately young flowers of *Helianthus* were, for many reasons, found to be the most suitable subject for the experimental purpose. In regard to the age of the specimen, freshly opened flowers are not very suitable; for their respiratory activity, though very considerable, does not remain uniform. When the flowers are about two days old they are, however, found to maintain a uniformity of respiratory activity for a considerable length of time. It may be said that such flowers when kept at a constant temperature of 32° C. were found to retain their respiratory

activity quite uniformly for a period of at least eight hours ; it may be stated here that the maximum time-limit of our experiment was well within that period.

Apparatus for the Measurement of Respiration

For measuring respiration the Automatic Respirograph devised and constructed in the Institute was used. A full description of the device has been published in our previous paper.[1] In this method the respiration is measured by the amount of oxygen consumed. The experimental material is put in the respiratory chamber, which is attached to a bubbler, through which pure oxygen is automatically drawn into the chamber in its consumption for respiration. The passage of each bubble, signifying a definite volume of the gas, is recorded on a moving drum by an electro-magnetic writer. The whole apparatus, excluding the drum and the electro-magnetic writer, is kept in a specially made electro-thermostatic chamber for the maintenance of a constant temperature. The rate of respiration is determined from the volume of oxygen consumed per unit time, the quantity being calculated after making proper allowance for normal temperature and pressure.

Method of Experiment

It has been previously mentioned that in recording respiration for any temperature, the temperature was maintained constant. For observing the effects of variation of temperature, the respiratory material was subjected to a particular temperature for a certain length of time, the effect at this temperature being recorded ; the temperature was changed to a different one and record taken once more. In this way, the effects induced at different temperatures were observed with a particular specimen. In subjecting the respiratory material to a different temperature, the thermostatic chamber and the respiratory chamber were carefully adjusted to the same temperature. As the respiratory chamber contained a large mass of alkali hydroxide solution its temperature could not be easily altered by only changing the temperature of the thermostatic chamber,

[1] Guha Thakurta and Dutt, 'An Automatic Respirograph,' *Trans. Bose Research Inst.*, vol. ix (1933–34), pp. 77–88.

since such an attempt is attended by a considerable waste of time. For minimising the time of experiment the procedure followed, when the effect of rise of temperature is to be studied, was to introduce a quantity of hot liquid into the chamber corresponding to the quantity taken so as to secure the desired rise of temperature. The temperature of the water contained in the specimen container was also changed in the same manner. About 15 minutes was required to produce a perfect thermal equilibrium between the different chambers. Another 15 minutes was allowed for the thermal adaptation of the specimen. After this period the record was taken for the next 30 minutes so as to obtain a satisfactory average value per minute. Thus for observing the effect at one definite temperature, about an hour was required.

Effect of Increase of Temperature on the Respiration of *Helianthus* Flower

It has been observed by a number of investigators that rise of temperature is accompanied by immediate or initial increase in the respiratory activity. Fernandes [1] in his investigation on the effect of temperature changes on the seedlings of *Pisum sativum*, concluded that for temperatures between 0° C. and 45° C., an increase of temperature results in an increase in the initial respiratory activity, but at temperatures above 45° C. there is progressive lowering of the initial rate. Kostytschew [2] came, however, to the conclusion that the rate of respiration gradually increases with the rise of temperature to a maximum value, at which it remains steady even with still higher rise of temperature until the thermal death point of the plant is reached.

In our experiments on the effect of rise of temperature on the initial rate of respiration of *Helianthus* flower, the experiments were performed in the months of March and April. The maximum temperature of the experimental room at the time was between 30° C. and 32° C. In the series of experiments to be presently described 32° C. has been taken as the normal initial temperature.

It may be thought that it would be desirable to record

[1] D. S. Fernandes, 'Aerobe und anaerobe Atmung bei Keimlingen von Pisum sativum.' *Rec. trav. bot. Neerlandais*, 20 (1923), 107–256.

[2] S. Kostytschew, *Pflanzenatmung*. Berlin, 1924.

the effects of rise of all degrees of increase of temperature in a single specimen. But this would have entailed the subjection of the specimen for an exceptionally lengthy period at higher temperatures. Such a procedure would have undoubtedly modified the normal tone of the specimen. In order to obviate this drawback the experiments on the effects of a wide range of temperature were carried out with a number of similar specimens. The effects of two or three definite rises of temperature were, however, observed in a single specimen. This had the advantage that the particular specimen was subjected to the rise of temperature for a comparatively short length of time which did not exceed more than three hours.

The specimens used for the different series of experi-

FIG. 44. Record of respiration of *Helianthus* flower at different rises of temperature, the duration of record in each series being 30 minutes.

a . . . . . at 32° C. (normal).
b . . . . . at 42° C.
c . . . . . at 50° C.

ments were quite similar, as was verified from their normal respiratory rate at 32° C. A constant weight of 25 grams of flowers, the average number of which was about eighteen, was taken for each experiment.

In our experiments on the effect of increase of temperature, it was observed that the respiratory rate increased with rises of temperature till a critical point was reached; above this point the rate of respiration underwent a noticeable decline. The effects of still higher temperatures were also observed when the respiratory rate exhibited continuous enfeeblement until its total cessation.

In order to arrive at a generalisation a very large number of experiments were carried out in this manner. As an example of the method employed we shall give certain typical examples. The first of the series of records is illustrated in fig. 44, in which series *a* represents the normal rate of respiration at 32° C.; the following series *b* and *c*

represent the rates at 42° C. and 50° C. respectively. In series *a* there are 40 dots, each representing the consumption of 0·3 c.c. of oxygen. The total volume of oxygen consumed in 30 minutes is $0{\cdot}3 \times 40 = 12$ c.c. at a temperature of 32° C. and at the atmospheric pressure of 75·46 cms., the value at the time of the experiment. The volume of oxygen (at N.T.P.) consumed per gram of the flower per minute is :

$$\frac{12 \times 75{\cdot}46 \times 273 \times 1000}{(273 + 32) \times 76 \times 30 \times 25} = 14{\cdot}22 \text{ c.mm.}$$

In series *b* there are altogether 68 dots, representing the consumption of $68 \times 0{\cdot}3$ c.c. of oxygen. The rate per minute is $\frac{68 \times 0{\cdot}3}{30}$ or 0·68 c.c. at a temperature of 42° C. and pressure 75·46 cms. Therefore the volume (at N.T.P.) of oxygen consumed per gram per minute is found by calculation to be 32·4 c.mm.

The result of experiments carried out at the temperature of 50° C. is illustrated in series *c*, in which there are recorded 99 dots in the course of 30 minutes. The volume of oxygen consumed is therefore $\frac{99 \times 0{\cdot}3}{30}$ or 0·99 c.c. per minute at a temperature of 50° C. and pressure of 75·46 cms. Therefore the volume (at N.T.P.) of oxygen consumed per gram per minute is found to be 33·23 c.mm.

The result of the above experiment may be tabulated as follows :

Temperature	C mm. (at N.T.P.) of oxygen consumed per gram per minute
32° C.	14·22
42° C.	23·40
50° C.	33·23

TABLE I.—EFFECT OF RISE OF TEMPERATURE ON THE INITIAL RESPIRATORY RATE OF *HELIANTHUS* FLOWER

Temperature in ° C.	C.mm. (at N.T.P.) of oxygen consumed per gram per minute	Temperature in ° C.	C.mm. (at N.T.P.) of oxygen consumed per gram per minute
32	14·136	44	25·876
33	15·012	45	27·136
34	15·700	46	28·480
35	16·332	47	29·732
36	17·208	48	31·372
37	18·128	49	32·996
38	19·340	50	34·096
39	20·388	51	36·780
40	21·296	52	39·064
41	21·836	53	9·876
42	23·584	54	4·672
43	24·772	55	1·972

Having described in detail the method of experiment and the value obtained in a typical experiment, the average values of respiratory activity as deduced from numerous experiments carried out at different temperatures are given in Table I. In regard to respiration at 55° C., it should be stated that the rate not only exhibits a very marked

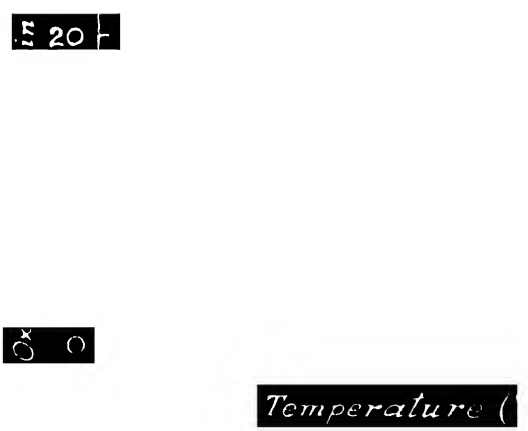

FIG. 45. Curve showing the effects of different rises of temperature on the respiration of *Helianthus* flower.

immediate depression but comes to a stop in the course of an hour.

The initial effect of rise of temperature on respiration is graphically represented in fig. 45, the data being supplied by Table I.

From the results of the above experiments it is clear

that the critical temperature-maximum for the initial effect of rise of temperature is 52° C., above which there is decline. Fernandes in his experiments with *Pisum sativum* also finds a critical temperature-maximum above which there is a decline. The results obtained by both ourselves and Fernandes thus appear to cast doubt on the conclusion of Kostytschew, who thought that the maximum rate is maintained unchanged till the death point is reached.

The temperature-maximum of *Pisum sativum* determined by Fernandes is 45° C., that is to say, seven degrees lower than that of *Helianthus* flower as observed by us. How to explain this difference ? The first series of our experiments, it is to be remembered, was carried out in the summer season with prevalent high temperature, and it is conceivable that this might have exerted some influence in raising the critical temperature. The question was subjected to further inquiry by carrying out investigations with *Helianthus* flower grown in the winter season, when the prevailing temperature was 25° C.

Effect of Rise of Temperature on Respiration of Flower of *Helianthus* grown in Winter

Helianthus can be grown at all seasons, though it is usually grown in Bengal from February to June. For the purpose of our present experiments plants were grown

Fig. 46. Record of respiration of *Helianthus* flower growing in winter at different rises of temperature.

a . . . . . at 25° C. (normal).
b . . . . . at 30° C.
c . . . . . at 35° C.
d . . . . . at 40° C.

early in winter, so that flowers appeared in January. The maximum temperature at that time did not exceed 25° C. We took care that the thermostatic chamber should be initially adjusted to 25° C. Records were taken at this as

well as at definite higher temperatures. A typical record is reproduced in fig. 46, which gives records of rates of oxygen consumption at three different temperatures besides that of the normal. Series *a* represents the normal rate at 25° C. and *b*, *c*, *d* at temperatures of 30° C., 35° C., and 40° C. respectively. The summary of the quantitative results thus secured is given below.

Temperature	C.mm. (at N.T.P.) of oxygen consumed per gram per minute
25° C.	7·724
30° C.	11·940
35° C.	16·372
40° C.	21·364

TABLE II.—EFFECT OF RISE OF TEMPERATURE ON THE INITIAL RESPIRATORY RATE OF *HELIANTHUS* FLOWER GROWN IN WINTER.

Temperature in ° C.	C.mm. (at N.T P.) of oxygen consumed per gram per minute	Temperature	C.mm. (at N.T.P.) of oxygen consumed per gram per minute
25	7·702	45	27·929
30	11·836	50	34·589
35	16·540	52	37·450
40	21·175	55	0·232

From the above results we find that the rate of normal respiratory activity at the prevailing lower temperature of 25° C. is relatively more sluggish than at the normal temperature of 32° C. in summer. But when the temperature was raised above that point, the rates did not differ from the corresponding ones in summer.

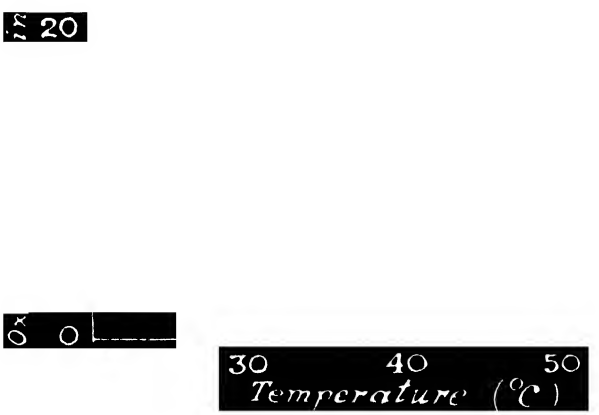

FIG. 47. Curve showing the effects of different rises of temperature on the respiration of *Helianthus* flower growing in winter.

The data obtained from a number of experiments are given in Table II.

From the data of Table II it will appear that, though acclimatised normally to lower temperature, the critical temperature-maximum in winter is the same as that in summer (*cf.* Table I). It would thus appear that adaptation

of the flowers to the condition of lower temperature induces no alteration in the critical temperature.

In fig. 47 is given a curve showing the relation between rises of temperature and respiration of *Helianthus* flower grown in winter.

We shall next describe the determination of the temperature coefficient of respiration of *Helianthus* flower.

Temperature Coefficient of Respiration

By the temperature coefficient, which is signified by the symbol Q_{10}, is meant the ratio of the rate of reaction at one particular temperature to the rate at a temperature 10° C. lower. In the case of purely chemical reactions that obey Van't Hoff rule, the velocity of reaction is increased from two to threefold by a rise of temperature of 10° C. Various attempts have been made by different observers in determining the connection between respiration and chemical reaction which obey Van't Hoff rule.

In regard to this question widely different opinions are entertained. Thus, for example, Krogh [1] is of opinion that it is inconceivable that temperature coefficient of respiration could follow Van't Hoff Law. For according to him the phenomenon was not determined by simple chemical reaction, but constituted a complex series of reactions taking place in a heterogeneous system.

There are others who are of opinion that there is a temperature coefficient for respiration, though there is difference of opinion in regard to the question whether this coefficient remains constant throughout a wide range of rise of temperature. Clausen [2] obtained the value for Q_{10} to be 2·5 in the cases of Wheat, Lupin seedlings and Syringa flowers between 0° C. and 20° C. Blackman and Matthaei [3]

[1] R. Ege and A. Krogh, 'Temperature and Respiratory Exchange in Fishes,' *Internat. Rev. d. ges. Hydrobiol. U. Hydrogeog.*, vol. 7 (1914), pp. 48–55.

[2] H. Clausen, 'Beitrage zu Kennthiss der Atmung der Gewachse und des pflanzlichen stoffwechsels,' *Landw. Jahrb.*, vol. 19 (1890), pp. 893–930.

[3] F. F. Blackman and Gabrielle L. C. Matthaei, 'Experimental Researches on Vegetable Assimilation and Respiration. IV.—A Quantitative Study of Carbon Dioxide Assimilation and Leaf Temperature in Natural Illumination,' *Proc. Roy. Soc.*, B, vol. 76 (1905), pp. 402–460.

Matthaei, Gabrielle L. C., 'Experimental Rsearches on Vegetable Assimilation and Respiration. III.—On the Effect of Temperature on Carbon Dioxide Assimilation,' *Phil. Trans. Roy. Soc.*, London, B, vol. 197, (1905), pp. 47–105.

obtained 2·1 as the value for Q_{10} in Cherry Laurel leaves over a temperature range from 16° C. to 45° C. There are, however, others who deny the constancy of the value of Q_{10} for higher temperatures, though they concede that at lower temperatures the coefficient obeys Van't Hoff rule fairly well. Thus Gerhart,[1] working with Strawberry fruits, obtained 2·5 as the value of Q_{10} between 5° C. and 25° C., but with temperatures above 25° C. he could not arrive at any constant value. Kuijper,[2] working with germinating Peas, found that Van't Hoff Law is followed up to 20° C., and above that the temperature coefficient fell off rapidly. Kanitz,[3] in analysing the relation of plant respiration and temperature, pointed out that Q_{10} is relatively higher for the lower range of temperature than for the higher range.

Assuming that there is a temperature coefficient, the difference of values, especially at higher temperatures, found by different observers may be accounted for from the following considerations. We found, as will be explained later, that the maximum rate at higher temperatures is not maintained for a long time but declines with time (*cf.* Table V). For the correct determination of the respiration rate at higher temperatures it is absolutely necessary to reduce the time of experiment to as short a period as possible. This problem has been very satisfactorily solved by the method employed by us in which by greatly reducing the period of experiment higher accuracy of results was assured. As examples of results thus secured we shall refer to Tables I and II, which summarise data of maximum rates at higher temperatures over a range of 25° C. to 55° C. For the exact determination of the nature of the temperature coefficient of respiration at higher temperatures, the Q_{10} values, separately calculated from the data given in Tables I and II, are given in Tables III and IV, and represent the values obtained for summer and winter specimens respectively.

[1] A. R. Gerhart, ' Respiration in Strawberry Fruits,' *Bot. Gaz.*, vol. 89, (1930), pp. 40–66.

[2] J. Kuijper, ' Uber den Einfluss der Temperatur auf die Atmung der hoheren Pflanzen,' *Rec. trav. bot. Neerland*, vol. 7 (1910), pp. 131–239.

[3] Aristides Kanitz, ' *Temperatur und Lebensvorgange*, Berlin, 1915.

TABLE III.—TEMPERATURE COEFFICIENTS OF RESPIRATION OF SUMMER SPECIMENS OF *HELIANTHUS* FLOWER AT VARIOUS TEMPERATURES

Temperature difference in ° C.	Q_{10} value	Temperature difference in ° C.	Q_{10} value
32–42	1·668	38–48	1·622
33–43	1·655	39–49	1·613
34–44	1·647	40–50	1·620
35–45	1·686	41–51	1·684
36–46	1·655	42–52	1·656
37–47	1·640		

TABLE IV.—TEMPERATURE COEFFICIENTS OF RESPIRATION OF WINTER SPECIMENS OF HELIANTHUS FLOWER AT DIFFERENT TEMPERATURES

Temperature difference in ° C.	Q_{10} value	Temperature difference in ° C.	Q_{10} value
25–35	2·147	35–45	1·688
30–40	1·789	40–50	1·633

In Table III, giving results obtained with summer specimens, the Q_{10} value varies between 1·61 and 1·68 over the range of 32° C. to 52° C. The average value of Q_{10} may

therefore be taken as 1·65. The results given in Table IV refer to winter specimens, in which case it has been possible to determine the value of the coefficients for relatively lower temperatures. The Q_{10} value between 25° C. and 35° C. is 2·1, which is fairly high and approaches that obtained by Blackman in Cherry Laurel leaves. The Q_{10} between 30° C. and 40° C. is 1·789, which shows that the value has fallen with the increase of temperature. The Q_{10} values exhibit further decline with still higher increase of temperature, being 1·688 and 1·633 respectively. It will be noted that these values of Q_{10} for winter specimens approach very closely to those of summer (*cf.* Table III).

In summarising the results it might be stated that at a range of temperature below 32° C. the Q_{10} value is distinctly higher than above that range, and that between 32° C. and 52° C. the Q_{10} value remains fairly constant.

Determination of the Optimum Temperature for Respiration of *Helianthus* Flower

In regard to the question of determination of optimum temperature for respiration, diverse views are entertained by different investigators. Kostytschew is of opinion that there is no optimum temperature above which the respiratory activity, as evidenced by the evolution of carbon dioxide, underwent a decline. In criticising this conclusion it may be urged that Kostytschew had not taken into consideration the influence of the time-factor in modification of respiration (*cf.* Table V). The results obtained by Fernandes appear to be somewhat different. He found that while the high initial rates at 45° C., 40° C., and 35° C. declined with duration of exposure to these temperatures, yet at 30° C. there occurred no falling off in the respiratory activity during the period of his observation In summarising these results Stiles[1] regarded the temperature in the neighbourhood of 30° C. to be the optimum for the experimental material under consideration.

In considering the problem, we have to bear in mind that since the respiratory material has to depend on a limited store of food reserve, the respiratory activity cannot remain constant for an indefinite length of time even at lower temperatures. It is bound to decline with

[1] W. Stiles and W. Leach, ' Respiration in Plants,' London, 1932.

time following the exhaustion of the limited amount of energy supply. The time-factor will thus always stand in the way of correct determination of the optimum temperature for respiration. In determining the optimum temperature, therefore, there is no alternative other than reducing the time-factor within a reasonably short limit.

TABLE V.—THE TIME-FACTOR IN MODIFICATION OF RESPIRATION OF *HELIANTHUS* FLOWER AT VARIOUS TEMPERATURES

Temperature in ° C.	C.mm. (at N.T.P.) of oxygen consumed per gram per minute			
	Initial	2nd hr.	4th hr.	6th hr.
25	7·688	7·688	7·688	7·688
30	11·488	11·488	11·908	11·908
32	14·176	14·176	14·528	14·176
34	15·720	15·720	16·080	16·080
35	16·480	16·830	17·204	14·696
40	21·056	21·056	16·932	11·736
52	38·440	38·836	8·400	2·004

In such circumstances the maximum temperature at which an enhanced rate is maintained for a fairly long period may be regarded as the optimum temperature for respiration of the particular specimen.

As the specimen of *Helianthus* flower was kept in water and without any food supply from outside, it had to depend entirely on its reserve stock within itself. Therefore in

determining its optimum temperature for respiration the time of observation was limited to the short period of six hours.

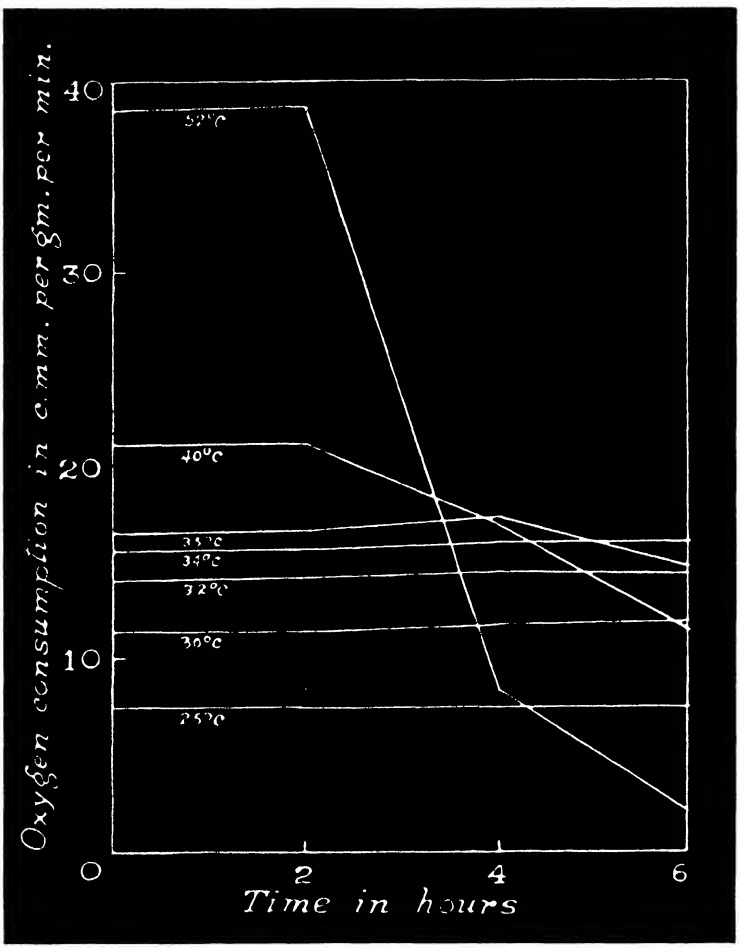

FIG. 48. Curves exhibiting the effect of time-factor in modification of respiratory activity of *Helianthus* flower at different temperatures.

The experiment was conducted in February, when the normal temperature of the experimental room did not exceed 25° C. This enabled observation of the effects of higher

temperatures from an initial temperature of 25° C. Records were taken at intervals of two hours. The temperature at which the maximum rate is maintained for six hours without diminution may therefore be regarded as the optimum temperature.

Table V gives the rates of respiration at definite temperatures, the observations being taken every two hours in succession, the total period being six hours. It will be noted that at the temperature of 25° C. the maximum rate did not undergo any diminution even at the expiration of six hours. The same is the case at the temperatures of 30° C., 32° C., and 34° C. At 35° C., however, while the initial rate was 16·480, it underwent a decline after the period of six hours. This decline is even more marked at higher temperatures of 40° C. and 52° C.

From the results given in Table V, as well as the curves given in fig. 48, it is clear that the maximum temperature at which prolonged exposure of six hours is not followed by any decline is 34° C.; this may therefore be regarded as the optimum for the respiration of *Helianthus* flower.

Effect of Decrease of Temperature on the Respiration of *Helianthus* Flower

Investigations were next carried out on the effect of decrease of temperature on the initial rate of respiration. In these experiments, the temperature was first raised from

FIG. 49. Record of respiration of *Helianthus* flower at different temperatures, showing the effect of decrease of temperature.
a . . . . . at 32° C. (normal).
b . . . . . at 50° C.
c . . . . . at 32° C.

normal to a higher value and then brought down to the lower ones.

A typical record exhibiting the effect of decrease of temperature is reproduced in fig. 49, in which the temperature was first raised to a higher value and then lowered to

the normal temperature. The first series of dots, *a*, 42 in number, shows the normal rate of respiration at 32° C., this being equivalent to the rate of 14·932 c. mm. (at N.T.P.) of oxygen consumption, per gram per minute. The second series of the record, *b*, was taken at 50° C.; there are now 100 dots, representing the rate of oxygen consumption of 33·58 c. mm. (at N.T.P.), per gram per minute. The third series, *c*, was recorded when the temperature was lowered from 50° C. to the normal 32° C. There are now 21 dots in this series, indicating a rate of 7·292 c. mm. of oxygen consumption (at N.T.P.), per gram per minute. The normal rate at 32° C., it will be remembered, is 14·932. But sudden return to the normal did not restore the normal rate of respiratory activity, for there was a considerable depression to 7·292, which is about half the normal rate. The normal rate was, however, found to be fully restored after a considerable length of time.

The effect of a sudden fall of temperature in returning from a higher to the normal is a diminished respiratory activity from which there is slow recovery to the normal.

Summary

The effect of variation of temperature on respiratory activity is subjected to modification by the time-factor, on account of which prolonged subjection to high temperature is attended by depression.

The drawback brought about by the time-factor is removed by the employment of the *Respirograph* specially devised for the investigation in which the period of time required for each determination is reduced to a minimum.

The experimental material employed for the investigation is the flower of *Helianthus annuus*. The results obtained show that the initial effect of rise of temperature is an enhancement of respiratory activity which increases with the rise of temperature till a maximum is reached at 52° C., this being the *critical temperature-maximum*.

Above this critical point, the rate of respiration undergoes a marked decline till there is a total cessation of respiration at death of the organism which occurs above 55° C.

The seasonal variation has no effect on the *critical temperature-maximum*, which therefore remains the same in plants grown either in summer or winter.

The temperature coefficient of respiration for the flower of *Helianthus* is found to be fairly constant over a range from 32° C. to 52° C., the value of Q_{10} being approximately 1·65. At lower range of temperature than above, the value of Q_{10} is comparatively higher, being as high as 2·1.

The *optimum temperature* for respiration was found from the determination of the particular temperature at which the maximum rate of respiration remains approximately constant for a fairly long period such as six hours. In *Helianthus* the *optimum temperature* is thus found to be at or near 34° C.

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VII.—CHEMICAL EXAMINATION OF THE INDIAN MEDICINAL PLANT *TRICHOSANTHES DIOECA*

BY

N. C. NAG, M.A., F.I.C.

Trichosanthes dioeca (Rox) is by far the most useful species of Trichosanthes cultivated in and around Calcutta and in certain parts of Bengal and Bihar. It is known in Sanskrit as *Putulika*, in Bengali as *Patal* and in Hindi as *Pulwal*. Suitable localities are those which are near rivers or canals, the soil having the advantage of getting silt deposits. Reference may be made to Roxburgh's 'Flora Indica'[1] for a full description of the botanical characters of the plant and its fruits.

The roots, the stems, the leaves and the fruits are largely used in the Ayurvedic or ancient Hindu system of medicine. Bhabprakash Misra[2] and others recommend the particular portions of the plant for any specific disease. The tender shoots, the leaves and the fruits, though bitter, are valued as wholesome food. The bitter principle,[3] however, is not the subject of investigation in this paper. The general method followed in the present investigation is the same as that used in examination of *Justicia Gendarussa* and of *Eupatorium Ayapana*.[4] The main inorganic constituents in the ash of the different parts have been determined. In some cases the nitrogen content of some of the parts has also been estimated. Further, a chemical examination of

[1] Roxburgh, *Flora Indica*, p. 694 (Ed. 1874).

[2] 'Bhabprakash,' translated by Debendra Nath Sen and Upendra Nath Sen, pp. 108, 109, 410. Charak, 'Chikitshitsthan,' chaps. 4, 12, 23, 24, 27. Susruta, 'Uttarkhanda,' chap. 45. Chakradatta, Fever Treatment (Jwarachiktsha) chapter.

[3] Dr. Chittaranjan Barat was also engaged in the Bose Institute in examining the bitter principle. To him and to Messrs. H. N. Banerjee and K. N. Bose my thanks are due for occasional help.

[4] *Trans. Bose Res. Inst.*, vol. vi (1930–31), pp. 203–211.

the soil suitable for growing the plant was carried out. The soil was also subjected to physical examination.

Patal Tuber and Ash Analysis

Though the plants are perennials, yet it is best to take out the tubers from the ground every two years for replantation, care being taken to plant a few tubers from male plants amongst the 95 to 98 per cent. of female plants. The tubers when first taken out of the ground are quite juicy and bitter. With the duration of drying they become more and more hardened, and can then be powdered. Tubers taken out of the ground from the Falta Experimental Field Station were immediately weighed (after cleaning from adhering earthy matter) and cut into thin chips and dried at 100° C. The amount of dry matter was 26·61 per cent.

Nitrogen was estimated and found to be from 0·84 per cent. to 0·90 per cent. of air-dry tuber; the percentage rose to 1·20 in tubers powdered and dried at 105° C.

The dry tuber substance after careful ashing is slightly flesh coloured. The amount of ash is about 5·4 per cent. of dry powdered tubers. The result works out to about 1·39 per cent. of the weight of freshly taken out tubers.

The results given below are the average results obtained with tubers taken from the market, as also from the experimental fields at Falta.

Results of Tuber Ash Analysis

SiO_2	4·31 per cent.
P_2O_5	26·78
SO_3	5·29
Cl	0·80
Al_2O_3	0·42
Fe_2O_3	2·42
MnO	0·10
MgO	7·60
CaO	10·10
K_2O	40·33
Na_2O	0·30
Total determined	98·45 per cent.

The difference from 100 is comparatively small There was scarcely any carbonate when properly ashed. The most significant figures are the high percentages of alkali

and phosphoric acid. The presence of 5·29 per cent. of SO_3 in the ash is also indicative of the large amount of sulphur compounds in the bulbs.

The *p*H value of the sap pressed out from fresh *Patal* tubers from Falta Fields was found to be 5·40.

Results of Stem-ash Analysis

The composition of the stem-ash varies within certain narrow limits according as the portion of the stem is taken from the upper or the lower end. The following is the result of a typical case of stem taken from between the fifth node and the twelfth node, counting from the upper end of the shoot.

In the case of the stem it is comparatively easy to get complete ashing even without any ashing furnace, an ordinary Bunsen being sufficient for the purpose. The amounts of the different constituents are given below, from which it will be seen that the phosphoric acid content is comparatively low.

SiO_2	14·25 per cent.
P_2O_5	5·78 ,,
SO_3	3·86 ,,
Cl	0·44 ,,
Al_2O_3	trace
Fe_2O_3	2·94 ,,
MnO	0·07 ,,
CaO	26·74 ,,
MgO	6·31 ,,
K_2O	17·32 ,,
Na_2O	16·52 ,,
Total determined	94·23 per cent.

The difference from 100 is higher than in the case of the analysis of tuber. Carbonate, which was practically absent in the tuber ash, is noticeably present in the stem ash. The most prominent constituents present are the higher percentages of lime and silica, with tendency towards equalisation in the proportion of the two alkalis—K_2O and Na_2O.

Results of Analysis of *Patal* Leaves

Patal leaves are extensively consumed as vegetable food, being reputed to be very suitable for convalescent patients.

The size and colour of the leaves vary a good deal according to their healthy condition of growth, in which condition the leaves are large in size and bright green in colour.

Leaves freshly plucked from the plants and dried at 100° C. give about 13·11 per cent. of matter, which when burnt gives about 16·5 per cent. of ash.

Leaves when left in the air become dry and light yellow in colour, the green colour of the chlorophyll being then destroyed; the bitter taste of the leaves is, however, still persistent.

Nitrogen was estimated and gave on dry matter basis the following results in different samples:

Nitrogen content = 4·06 per cent., 4·07 per cent., 4·12 per cent., 4·19 per cent.

It will thus be seen that the nitrogenous constituents in the leaves are fairly high in all the different samples examined.

The examination of ash from leaves was undertaken with samples from Calcutta and also those from Falta Field Station. The results of analyses are given side by side for comparison:

RESULTS OF ASH ANALYSIS OF LEAVES

	Calcutta specimen	Falta specimen
SiO_2	46·37 per cent.	35·10 per cent.
P_2O_5	4·07 „ „	6·31
SO_3	3·32	3·65
Cl	4·70	5·33
Fe_2O_3	1·90	1·92
MnO	0·07	0·07
MgO	6·80	9·25
CaO	21·68	22·55
K_2O	5·15	6·70
Na_2O	5·40	6·95
Total determined	99·46 per cent.	97·83 per cent.

The silica content in the ash of *Patal* leaves is very high. The total alkali portion in the leaves, in comparison with that in tubers, is considerably less, while Na_2O is slightly more in quantity than K_2O. The Falta samples of leaves are comparatively rich in magnesium and sodium chlorides but poor in silica.

I shall now digress to describe the results of chemical examination of the leaves of *Nyctanthes arbortristis* (Linn.),

known in Bengali as *Shefalika*,[1] which according to Hindu medicine [2] is supposed to have medicinal properties similar to those of leaves of *Patal*. The two plants *Patal* and *Shefalika* are widely different in characteristics in the sense that *Shefalika* is a tree growing to a height of 20 feet or more, whereas *Patal* is a creeper. In view of the similar medicinal characteristics I thought it would be interesting to give the results of analysis of ash of leaves of *Shefalika* with a view to comparing the results with those already obtained with leaves of *Patal*.

CHEMICAL EXAMINATION OF LEAF ASH OF *NYCTANTHES ARBORTRISTIS*

Five leaves of freshly plucked *Shefalika* weighing 10 grams were obtained from a tree growing in the Bose Institute Garden, and when dried at 100° C. gave 2·349 grams of dry matter.

The ash content of dry leaves varied from 12·20 to 13·79 per cent. The older leaves generally gave higher ash content with more SiO_2 and less P_2O_5.

Nitrogen in dry leaf matter was found to be 3·96 per cent. to 3·94 per cent.

Results of two typical samples are given below:

SiO_2	47·31 per cent.	44·77 per cent.
P_2O_5	4·05 ,, ,,	5·38
SO_3	0·84	1·40
Cl	0·76	0·60
Fe_2O_3	1·16	2·00
MnO	0·07	0·07
MgO	7·03	6·80
CaO	16·70	15·20
Alkali	22·00	22·00
Total determined	99·92 per cent.	98·22 per cent.

A comparison of the results obtained shows that there is not much difference between the *Patal* and *Shefalika* leaves in their nitrogen, SiO_2, P_2O_5, iron, manganese and magnesium contents. *Patal* leaves, however, are richer in

[1] Roxburgh, *Flora Indica* (Ed. 1874), p. 29.

[2] Ayurved Sangraha, translation by Debendra Nath Sen and Upendra Nath Sen., p. 194. Chakradatta—chapter on fever treatment, *et seq.* Banaushadhidarpan, by Biraja Charan Gupta.

chlorine, sulphur and lime, while they are poorer in total alkali.

Like the leaves of *Patal*, the *Shefalika* leaves contain a bitter principle which is now under investigation.

Proceeding with the account of the chemical examination of *Patal*, I shall now deal with its fruit.

Examination of the Fruit of *Patal*

The size of the fruits varies considerably according to the variety of the plant and the habitat in which it has been grown. Usually the fruits are 14 to 16 cm. long with a girth averaging 6 to 9 cm. The ash is generally clear white with slight pure greenish spots indicating concentration of manganese in certain places, particularly where the seeds happen to be. The amount of ash from a fruit varied from 0·31 to 0·47 per cent. of the total weight of the fruit. The following gives a statement of typical results of fruit-ash analysis :

Results of Analysis of Patal Fruit Ash

SiO_2	3·82 per cent.
P_2O_5	16·44 ,, ,,
SO_3	5·58 ,, ,,
Cl	8·18 ,, ,,
Fe_2O_3	1·74 ,, ,,
MnO	0·06 ,, ,,
MgO	8·70 ,, ,,
CaO	13·80 ,, ,,
K_2O	34·85 ,, ,,
Na_2O	6·35 ,, ,,
Total determined	99·52 per cent.

An examination of the results of analysis shows the presence of considerable amounts of alkali, chlorine, sulphur and phosphorus.

The peculiarities in the constituent chemical substances in different parts of *Patal*, in roots, stems, leaves and fruits, may probably be associated with their supposed medicinal properties. The bitter principle, it is to be remembered, is also present in different parts of the plant.

I next take up the examination of the soil suitable for the growth of the plant *Patal*, both from the chemical and the physical standpoints.

CHEMICAL COMPOSITION OF THE SOIL FOR GROWTH OF *PATAL*

As already remarked, the *Patal* plant is grown only in certain provinces and in certain localities near rivers or natural canals. It is therefore likely that the soil has certain specialities in physical and chemical composition. The following refers to the soil of the experimental station at Falta.

A statement of the chemical constituents in the air-dry soil, passed through a 2 mm. round hole sieve, taken from the Falta Field Station, is given below:

Moisture determined at 105° C.	4·19 per cent.
Loss on ignition at 1000° C.	5·71
SiO_2 and insolubles	56·00
Fe_2O_3	10·28
Al_2O_3	14·06
CaO	1·35
MgO	0·80
MnO	0·11
P_2O_5	1·18
Alkali ($K_2O + Na_2O$)	3·60
SO_3	0·87
Cl	0·12
Total determined	98·27 per cent.

Total Nitrogen in the air-dry soil was estimated and found to be 0·184 per cent.

The loss on ignition gives an idea of the amount of carbonaceous matter in the soil, from which the ratio of carbon to nitrogen may be estimated. The amount of carbon was determined by wet combustion also. The ratio was found to be 10 to 1. It seems from this ratio that the soil is suitable also for the growth of *rice*. And indeed the Falta locality is considered to be good as a *rice-growing area*.

PHYSICAL PROPERTIES OF *PATAL* GROWING SOIL

The chemical composition of a soil as a whole, although it indicates its suitability for a particular crop, is not always a correct criterion unless the physical condition of the soil be also taken into consideration. For, even though the

mineral constituents necessary for the crop be present, yet they may not be so easily assimilable unless the soil be suitably disintegrated. This seems particularly to apply to the cultivation of *Patal*.

The following gives results of physical examination carried out according to modern British standards.[1]

The *p*H value of the Falta soil was found to be 5·5 to 6·0.

Fully air-dry soil at room temperature was first passed through a 2 mm. round hole sieve. This left only *0·90 per cent. of stones and gravel* on the sieve.

The portion that passed through the sieve was then further examined and gave the following results :

Moisture content at 105° C. . . 4·19 per cent.

Twenty grams of air-dry soil was treated with H_2O_2 to destroy organic matter and for the purpose of disintegration according to British standard methods, and finally treated with about 200 c.c. of N/15 HCl, stirring for one hour. The soil was then filtered and washed three times, each time with 100 c.c. distilled water. The filtrate was treated with ammonium chloride and ammonium hydroxide, which brought about the precipitation of mixed sesquioxides and silica, which were filtered, ignited and weighed.

The ignited and weighed precipitate came to 0·2900 gram.

This works out to *1·49 per cent. and is designated as "Loss by solution."*

The portion of the soil still remaining on the filter paper was then washed down with hot distilled water on to a wire sieve, aperture 0·2 mm. The residue on the sieve after drying and weighing was found to be 0·0255 gram. This works out as

"Coarse sand" . . . 0·1275 per cent.

The portion of the soil that passed through the 0·2 mm. sieve was transferred to a 1-litre shaking-bottle and made up to 500 c.c. with distilled water, to which was added 50 c.c. of "10 per cent. ammonia." This was then shaken vigorously for 12 hours. The suspension was then trans-

[1] 'Revised Official Method for Mechanical Analysis of Soils,' *J. Agric. Sc.*, vol. 18 (1928), pp. 734–39. 'The Physical Properties of the Soil,' by Bernard A. Keen (1931). The Rothamsted Monographs on Agricultural Science.

ferred to a *litre measuring cylinder,* and subjected to mechanical analysis in the following manner :

MECHANICAL ANALYSIS OF THE DISPERSED SUSPENSION

The first sampling was made at 10 cm. depth after the well-shaken suspension had stood for 4 minutes 48 seconds. A 20 c.c. pipette with top closed was lowered vertically to the indicated depth (10 cm.) and 20 c.c. of suspension drawn out, the actual drawing being begun 20 seconds before the expiry of the time (4 minutes 28 seconds). The suspension was delivered into a weighed platinum basin, dried at 105° C. and finally weighed to constant weight. This was found to be 0·2415 gram.

The percentage of material having a *settling velocity* of less then 10/288 = 0·0347 cm. per second (Stokes' Law) works out to :

$$\text{"}\textit{Silt} + \textit{Clay}\text{"} = \frac{100 \times 0{\cdot}2415 \times 100}{20 \times 20} = 60{\cdot}375 \text{ per cent.}$$

The next procedure was to *shake* the contents of the cylinder for *one minute* and then allow it to *rest for* 8 *hours.* A sample of 20 c.c. was again taken out, following the previous technique of drawing the suspension at 10 cm. depth from the new level. The weight of this portion after drying at 105° C. was found to be 0·0810 gram. Whence "Clay" works out to :

"*Clay*" . . . . 20·25 per cent.

The residual sediment left in the cylinder after clay sampling was transferred to a beaker after pouring off the supernatant liquid and made up to a height of 10 cm. above the base of the beaker with water. The whole liquid with the sediment was then stirred and allowed to settle for 4 minutes 28 seconds, and the turbid suspension poured off. The beaker was filled with water to the mark, stirred, allowed to rest for 4 minutes 28 seconds, turbid liquid poured off, etc., the procedure being repeated until the liquid was no longer turbid. This took 2 hours and a half. The residue was than collected, dried and weighed. The weight of the residue after drying was found to be 4·5875 grams or 22·99 per cent. of the original 20 grams of the soil we started with. This is shown as :

"Fine sand by sedimentation" = 22·99 per cent.

Summarising the results of Physical Analysis, we thus get the following :

Moisture loss at 105° C.	4·19	per cent.
Loss by ignition at 1000° C.	5·71	,, ,,
Loss by solution	1·45	,, ,,
Coarse sand	0·128	,, ,,
Clay	20·25	,, ,,
Silt	40·125	,, ,,
Fine sand by sedimentation	22·99	,, ,,
Total determined	94·84	per cent.

To this must also be added loss of other soluble constituents such as alkali, chlorides and sulphates which were present in the soil, and also calcium carbonate which must have been acted upon and brought into solution when the soil was treated with dilute hydrochloric acid after disintegration by H_2O_2 treatment. It will thus be seen that the soil is in a condition from which the plants are able to avail themselves of the constituents.

Summary

Trichosanthes dioeca (*Patal*) is a medicinal plant whose different parts are prescribed in the Hindu system of medicine for treatment of different diseases. The plant contains a bitter principle in all its different parts—roots, stems, leaves and fruits.

Chemical examination of the different parts of the plant shows certain characteristic variations in the proportions of the mineral constituents present. In the tubers there is a high percentage of the alkali K_2O as also a high percentage of phosphoric acid. In the stem there is present a high percentage of lime and an almost equal proportion of K_2O and Na_2O. The leaf ash is characterised by the presence of a high percentage of silica and lime. In the fruit there is a very high percentage of K_2O and moderately high percentages of lime and phosphoric acid and very little of silica.

Nitrogen has been estimated in the roots and the leaves on dry matter basis. While in the roots the amount is only 0·9 per cent. or so, the amount in the leaves is as high as over 4 per cent.

The contents of the leaves of *Shefalika* (*Nyctanthes arbor-*

tristis) have been compared with those of *Patal*. Like *Patal*, *Shefalika* leaves contain a bitter principle. Nitrogen, silica and some of the other constituents in the leaves of the two plants are nearly the same and comparable.

A chemical and physical examination of the soil suitable for cultivation of *Patal* has also been carried out. The carbon to nitrogen ratio in the soil is about 10 to 1. The soil is silty and is also suitable for the growth of rice.

I take this opportunity of expressing my grateful thanks to Sir J. C. Bose for his constant interest and helpful criticism during the investigation, and in drawing up the paper.

VIII.—EXAMINATION OF SEEDS OF CERTAIN VARIETIES OF MECONOPSIS AS SOURCE OF OIL AND MANURE

BY

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THE common poppy, *Papaver somniferum*, has been the subject of extensive investigation from time to time by many investigators, particularly as the source of opium bases. The oil content of the ripe seeds of *Papaver somniferum* is very high. Dr. Leather[1] found the oil content as high as 48·95 per cent. of the seed weight. The seeds are wholesome food; though the carbohydrate content is low, the albuminoid nitrogen is fairly high, being about 2·84 per cent., the total nitrogen being 2·97 per cent. A very complete account as regards the importance of poppy cultivation in India is to be found in Watt.[2] Lewkowitsch[3] in his classical work on Oils, Fats and Waxes deals with the characteristics of poppy oil and of its importance from the economic point of view.

Meconopsis as a class is allied to *Papaver somniferum*, being popularly known as Himalayan Poppy. *Meconopsis grandis* is described by Prain[4] as having been collected from Jongri, in Sikim, where it was brought probably from Nepal. The oil content is high, the oil being obtained by expression. Mr. Biren Ghose, to whom we are indebted for the collection and supply of seeds and plants for our experiments, assures us from his personal visit to Jongri, 14,000 feet above sea-level, that the cowherds who go there to graze their cattle during the summer months use the oil for cooking

[1] Leather, *Agricultural Ledger*, 1903, No. 7.

[2] Sir George Watt, 'Commercial Products of India, pp. 845–61.

[3] Lewkowitsch, 'Oils, Fats and Waxes,' vol. ii (1922), pp. 121 *et seq.* Also 'Laboratory Companion to Oils, Fats and Waxes' (1901), p. 42, Table 24A.

[4] Prain, 'Annals of the Royal Botanic Garden, Calcutta,' vol. ix, Pt. II.

purposes, the oil being quite palatable. The plant stalk is much relished and sought after by both men and animals.

The different varieties of Meconopsis that will be dealt with in our investigation under three divisions, I, II, III, are generally high-altitude plants which flower about July, the pods ripening by October. The seeds falling from the pods get covered by snow during the winter; they germinate and grow leaves during the next summer. The seedlings,

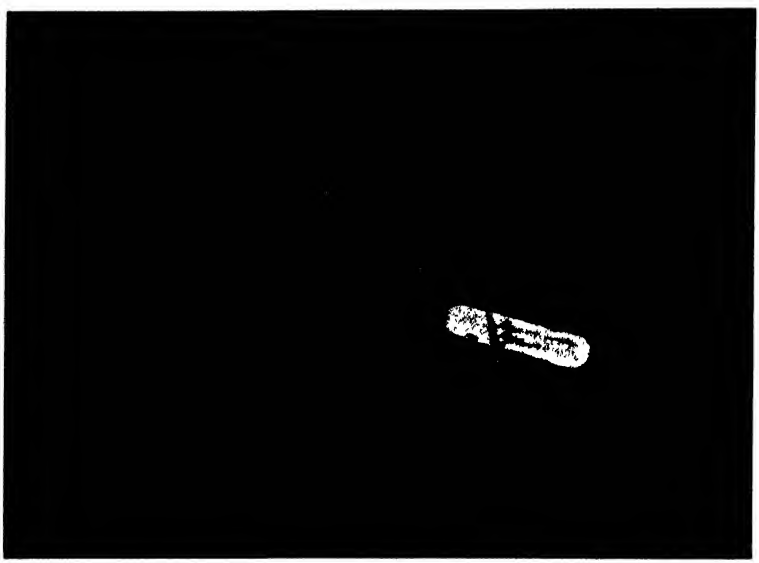

FIG. 50. *Meconopsis grandis*. Darjeeling.

scarcely above ground, get covered over with snow during the winter. The stalks of the plants grow to about five feet high by July, when they flower. It therefore takes two years for the plant to go through its life-cycle. Though there is no prolonged fall of snow at Darjeeling, yet it has been possible to grow some of the varieties at this lower altitude.[1] In certain cases, where germination had been

[1] We take this opportunity of thanking Mr. Biren Ghose for undertaking the growth of these and other varieties of Meconopsis in his plot of land at Darjeeling near Victoria Falls situated at a height of 6000 feet. Mayapuri Research Station, at about 7000 feet, has also some of these plants in growing condition.

delayed, it occurred when the sown seeds had been kept under powdered ice for a length of time.

We give on p. 126 a reproduction of the growing plant from a photo of *Meconopsis grandis* obtained on October 23, 1935, the plants being grown near the Victoria Falls, Darjeeling, at a height of 6000 feet.

In the present paper we shall deal with the seeds of and the oils obtained from (I) *Meconopsis napaulensis*, (II) *Meconopsis paniculata* and (III) *Meconopsis Wallichii*. It may be noted once for all that the pods of these Meconopsis are *villous*, while the pods of *Papaver somniferum* are *glabrous*. The seeds are generally small and darkish in colour.

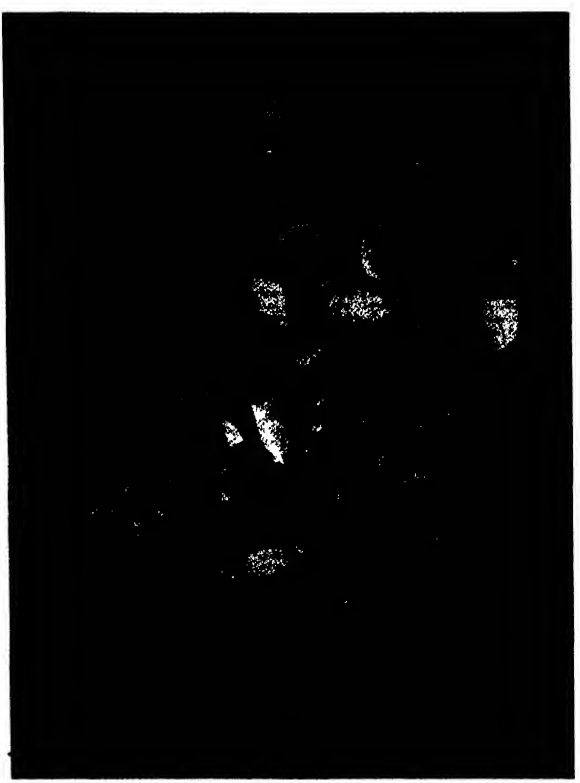

FIG. 51. *Meconopsis napaulensis*. Darjeeling.

I. *Meconopsis napaulensis*

Meconopsis napaulensis, D.C., is a strikingly beautiful plant which bears either dark purple or golden-yellow flowers. It occurs in large numbers at Sandakpu, in open places, at an approximate height of 12,000 feet. The number of valves in the pods varies from 5 to 7.

We give on p. 127 a reproduction of a photograph which we obtained of a bed of *Meconopsis napaulensis* specially grown for us at Darjeeling.

The roots of this plant are supposed to possess a narcotic property.[1] The seeds of the plant for examination were kindly collected for us by Mr. Ghose between Tonglu (height 10,120 feet) and Jongri (height 14,000 feet).

Examination of Seeds of (I) *Meconopsis napaulensis*

The seeds were examined for their oil content, also for their nitrogen and ash contents. The oil and the ash were then more thoroughly examined. The air-dry seeds were first crushed and then submitted to detailed examination. We undertook our examination with fresh specimens of seeds.

The results given below, unless otherwise mentioned, are on the basis of total seed weight.

Moisture in crushed seed	Oil by ether extraction	Ash
8·07 per cent.	26·22 per cent.	8·80 per cent.

Ash was determined in the original seed before and after extraction of the oil. The percentage of ash is calculated on the total seed weight basis.

Total nitrogen in the residue left after oil extraction was determined in the usual way and found to vary between 3·7 per cent. and 3·8 per cent. This indicates a high protein content, and also its value as a manure.

[1] Bose and Kirtikar, 'Indian Medicinal Plants.'

Results of Analysis of the Ash

The results appended below give a summary of average mineral constituents found in the ash.

SiO_2	5·61 per cent.
P_2O_5	33·44
CaO	24·52
Fe_2O_3	1·55
MnO	0·16
MgO	0·89
Cl	0·75
SO_3	1·50
Alkali ($Na_2O + K_2O$)	23·00
Total determined	91·42 per cent.

The total amount of mineral constituents determined thus came to about 92 per cent. of the ash. CO_2 and the undetermined portion amounted to about 8 per cent. The high percentage of P_2O_5 available in the residue after extraction of the oil from the seed would thus come to about 3·0 per cent.

Similarly the lime and the alkali in the total seed weight came to about 25 per cent. each. So that after extraction of the oil, the residue contained still higher percentages of lime, alkali, nitrogen and phosphoric acid, indicating a high manurial value of the oil cake.

Examination of the Oil

The oil as first extracted and freed from ether and water is transparent and of light yellow colour. Kept in stoppered glass bottles, even in diffused sunlight, the oil gets bleached and becomes colourless.

The following physical constants were determined:

Specific gravity at 30° C.	0·9180
Coefficient of expansion between 30° C. and 98° C.	0·000612
Refractive Index of freshly prepared oil at 30° C.	1·4731

In contact with air or with access to air even through a capillary bore glass stopper, the oil quickly absorbs oxygen and gets thickened, with rise in Refractive Index.

Chemical Examination

The results were obtained as the average of several determinations in different samples:

Oil yield in per cent. of seed weight	Saponification value	Iodine value	Acid value	R.M. value
26·22	187–181	130·3	40·6	0·21

The oil was saponified and free acids liberated by the usual methods. The amount of *unsaponifiable matter* found was as low as 0·62 per cent.

The results of examination of the free acids are given below:

Insoluble fatty acid	Iodine value	Refractive Index at 31° C.	Melting point	Solidifying point	Neutralisation value	Mean molecular weight
95·1 %	135	1·4633	19° C.	16° C.	191	293·2

The mixture of free fatty acids was separated into solid and liquid components by two different methods.

Separation by Fachini and Dorta's Method

The above method as modified by de Waele[1] gave the following results:

Per cent. of solid acid			Per cent. of liquid acid	
17·3			83·7	
Iodine value	Melting point	Solidifying point	Iodine value	Refractive Index at 31° C.
62·06	45° C.	43·5° C.	140	1·4678

[1] Lewkowitsch, 'Oils Fats, and Waxes,' vol. i (1921), p. 561.

The high iodine value of the solid portion of the separated acid mixture evidently points to the method of separation, which is not wholly satisfactory. A portion of the original mixture was, therefore, treated by Twitchell's process, the following results being obtained.

RESULTS BY TWITCHELL'S METHOD

Per cent. of solid acid			Per cent. of liquid acid	
23·0			76·1	
Iodine value	Melting point	Solidifying point	Iodine value	Refractive Index at 31° C.
37·5	45° C.	42° C.	140	1·4678

This process showed a slightly decreased yield of solid acid with a somewhat lower iodine value. But as the improvement in separation was not very marked, the original oil was again retested for its iodine value. It was now found that the original iodine value of the oil, 130·3, had come down to 116. It is thus evident that the oil was absorbing oxygen very rapidly and was undergoing continual change in composition. This was also evident from the increase in weight from day to day of a quantity of oil kept in a beaker inside a desiccator. Five and a half grams of oil went on increasing in weight at the approximate rate of 0·007 grams in 24 hours. In one instance the increase in 5·5 grams of oil in less than two hours at about midday was 0·0004 grams. The drying quality of the oil is indeed very high.

EXAMINATION OF THE LIQUID UNSATURATED ACID MIXTURE

With a view to obtaining a further insight into the composition of the liquid portion of the acid mixture, a quantity of the freshly prepared and separated liquid acid mixture was brominated according to usual method as recommended

by Eibner and Muggenthaler[1] (Bromine in Ether Solution at −10° C.). The amounts of di-bromide, tera-bromide and hexa-bromide formed were estimated and found to be:

Three grams of the acid gave—

Oleic Di-bromide	1·600 grams
Linolic Tetra-bromide . . .	3·960 ,,
Linolenic Hexa-bromide . .	0·222 gram

Interpreting the above figures in terms of the corresponding acids, we get:

	Grams	Per cent. obtained
Oleic Acid	1·021	34·03
Linolic Acid . . .	1·848	61·60
Linolenic Acid . . .	0·0833	2·78
Total unsaturated acid obtained . . .		98·41

Examination of Seeds of (II) *Meconopsis paniculata*

Meconopsis paniculata bears, like *Meconopsis napaulensis*, beautiful blue flowers in the month of July and the stalks grow to a height of about 5 feet. The number of pods in *M. paniculata* generally varies from 8 to 11.

A reproduction of a photograph of a bed of *M. paniculata* grown at Darjeeling for our experiments is given on p. 133.

The seeds were kindly collected for us by Mr. B. Ghose at Tonglu, Talung (Sikim, height 13,000 feet), and above Lake Chhangu (height 13,000 feet).

The experimental procedure was similar to that of *M. napaulensis*. The following is a statement of results obtained with fresh seeds.

Moisture in crushed seed	Oil by ether extraction	Ash
9·47 per cent.	32·50 per cent.	4·45 per cent.

Total Nitrogen in the residue after extraction of the oil was determined and found to be 3·81 per cent., indicating as in the previous case a high protein content.

[1] Lewkowitsch, 'Oils, Fats and Waxes,' vol. i (1921), p. 585.

FIG. 52. *Meconopsis paniculata.* Darjeeling.

RESULTS OF ANALYSIS OF THE ASH OF SEEDS OF *MECONOPSIS PANICULATA*

SiO_2	13·81	per cent.
P_2O_5	26·61	,,
Cao	21·22	,,
Fe_2O_3	1·10	,,
Mno	0·50	,,
Mgo	1·68	,,
Cl	0·80	,,
SO_3	2·38	,,
Alkali ($Na_2O + K_2O$)	23·66	,,
Total determined	91·76	,,

As in the case of *Meconopsis napaulensis* the total mineral constituents determined in ash comes to about 92 per cent. The oil obtained from fresh samples of seeds is very considerable, being about one-third of the seed weight. The seeds of *M. paniculata* thus appear to be a promising source of supply of oil. Considering the various uses of common poppy seed oil, as detailed in Lewkowitsch,[1] the seeds of *M. paniculata* may prove to possess some economic importance. The P_2O_5 as well as the nitrogen contents are also fairly high.

Examination of the Oil from Seeds of *Meconopsis paniculata*

The colour of the oil is somewhat similar to that of the oil of *M. napaulensis*, and is readily bleached by sunlight. The oil easily absorbs oxygen; a dropping-bottle half filled with oil, left over for about a year with only a capillary opening, gets so thickened that it may be put upside down for a few minutes without any danger of the oil trickling down.

The following physical constants were determined:

Specific gravity at 26° C.	0·9212
Coefficient of Expansion between 26° C. and 98° C.	0·00063
Refractive Index at 32° C.	1·4735

Results of Chemical Examination

Oil yield in per cent. of seed weight	Saponification value	Iodine value	Acid value	Unsaponifiable matter
32·5	187	125·2	32	1·06

The only noticeable difference in the above values from those obtained for *Meconopsis napaulensis* are the higher acid value and slightly higher quantity of unsaponifiable matter.

[1] Lewkowitsch, 'Oils, Fats and Waxes,' vol. ii (1922), p. 121.

The following figures give the values obtained for the free fatty acid mixture :

Per cent. of insoluble free fatty acid	Iodine value of acid	Refractive Index at 32° C.
95·4	128	1·4643

The free fatty acid mixture was separated into liquid and solid portions by Twitchell's process and the following results obtained :

Per cent. of solid acid			Per cent. of liquid acid	
18·89			81·11	
Iodine value	Melting point	Solidifying point	Iodine value	Refractive Index at 30° C.
10·58	51° C.	49° C.	151·13	1·4678

It will be seen from the iodine values determined, that the separation into solid and liquid acid portions has been more thorough than in the case of *M. napaulensis*.

Examination of the Liquid Unsaturated Acid Mixture

As in the case of the liquid acid mixture obtained from *Meconopsis napaulensis*, the liquid unsaturated acid mixture obtained from *M. paniculata* oil was further treated by the Eibner Muggenthaler process, and the following is a short summary of the results.

Three grams of the liquid acid gave :

Oleic Di-bromide . . . . 1·2 gram
Linolic Tetra-bromide . . . 4·5 grams
Linolenie Hexa-bromide . . . Nil

It will be seen that no hexa-bromide was obtained. The tetra-bromide obtained gave the melting point of 114° C. to 115° C., a fair indication of its purity.

Interpreting the above figures in terms of the corresponding acids, we get :

Linolic Acid	70·0 per cent.
Oleic Acid	25·5 ,,
Total unsaturated acid obtained .	95·5 ,,

The most noticeable fact is the absence of linolenic acid.

Examination of Seeds of (III) *Meconopsis Wallichii*

Meconopsis Wallichii is the familiar blue poppy of Sikim, and bears pale blue flowers. It is quite plentiful at Tonglu

Fig. 53. *Meconopsis Wallichii.* Tonglu.

at a height of 10,120 feet, and grows almost side by side with Aconite plants. It is remarkable that the cattle of the locality, which go there only during the summer months, avoid the poisonous Aconite almost by instinct. The stalk is often more than six feet in height. As with other varieties of Meconopsis in these parts, the plants are eaten by the grazing cattle and also by the cowherds, making it difficult to obtain suitable specimens for examination. A

small plot of land at Tonglu was, therefore, kept surrounded by fencing under the care of a local constable. Below is reproduced a portion of the experimental plot with stalks of *M. Wallichii* some of which are more than six feet in height. The ripe pods are usually 5 to 7 valved.

The higher altitude plants, as previously stated, have been successfully grown for us at the lower altitude of Darjeeling. The photographs of young and fully grown

FIG. 54. *Meconopsis Wallichii.* Darjeeling.

specimens of the plant which we obtained are here reproduced.

We worked with seeds of *Meconopsis Wallichii* collected at Tonglu the previous year and also with the seeds taken from one of the plants grown at Darjeeling.

The procedure followed was the same as in the case of other varieties of Meconopsis. The results are given below.

TONGLU SEEDS COLLECTED IN 1934

Moisture in whole seeds	Oil by ether extraction	Ash
5·8 per cent.	34·20 per cent.	5·00 per cent.

Total Nitrogen in the residue after extraction of the oil was determined and found to be 3·14 per cent. of the residue.

DARJEELING SEEDS FRESHLY COLLECTED

Moisture in whole seeds	Oil by ether extraction	Ash
4·88 per cent.	43·95 per cent.	6·20 per cent.

Total Nitrogen in the residue after extraction of the oil was determined and found to be 4·88 per cent.

As the result of analysis of ash of *Meconopsis Wallichii* seeds, the same characteristic of high value for P_2O_5, CaO and alkali ($Na_2O + K_2O$) was noticeable. The average values were as follows:

P_2O_5	34·95 per cent.
CaO	23·53 ,,
$Na_2O + K_2O$ . . .	23·70 ,,

EXAMINATION OF THE OIL FROM SEEDS OF *MECONOPSIS WALLICHII*

As in the case of the oils from the other species of Meconopsis dealt with in this paper, oil from *Meconopsis Wallichii* is also light coloured. In this case, too, the absorption of oxygen is quite rapid, and the iodine value of the oil undergoes a rapid diminution.

The following physical constants were determined for the oil extracted from Tonglu seeds:

Specific gravity at 28 °C.	0·93205
Coefficient of expansion between 28–100 °C. .	0·000716
Refractive Index at 28 °C.	1·4753

RESULTS OF CHEMICAL EXAMINATION

Oil	Saponification value	Iodine value	Acid value	Unsaponifiable matter	R.M. value
Per cent. 34·20	182·2	128·7	14·2	Per cent. 0·91	8·32

The most noticeable characteristic differentiating this oil from the others dealt with here is the large quantity of soluble volatile fatty acid (R. M. value).

The following figures give the values obtained for the free fatty acid mixture:

Insoluble free fatty acid	Iodine value of the acid mixture	Refractive Index at 25° C.
94·88 per cent.	132·7	1·4715

The free fatty acid mixture was then separated into solid and liquid components by Twitchell's process, and the following results obtained:

Solid Acid				Liquid Acid		
Yield per cent.	Iodine value	Melting point	Solidifying point	Yield per cent.	Iodine value	Refractive Index at 26·5° C.
12·0	12·07	48° C.	46° C.	88·0	145·96	1·4715

As in the case of *Meconopsis paniculata* the separation into solid and liquid acids was better than in *M. napaulensis.*

Examination of the Liquid Unsaturated Acid Mixture by Bromination

The liquid acid portion obtained from *M. Wallichii* on being brominated according to the Eibner and Muggenthaler process gave the following results :

Amount of liquid acid taken .	1·373 gram
Oleic Di-bromide obtained .	0·730 gram
Linolic Tetra-bromide obtained	1·800 gram, M.P. 112°–113° C.
Linolenic Hexa-bromide obtained	0·080 gram, M.P. 177°–178° C.

From the above figures the amounts of oleic, linolic and linolenic acids were calculated :

Oleic Acid	33·92 per cent.
Linolic Acid	61·18 ,,
Linolenic Acid . . .	1·75 ,,

Summary

The quantities of oil obtained from different species of Himalayan Meconopsis seeds growing at high altitudes have been determined. The residues left after oil extraction have also been examined chemically by estimating the different constituents present in them, particularly the amounts of total nitrogen, phosphoric acid and alkali, which are fairly high in every case.

It has been possible to grow some of the species with advantage at somewhat lower altitudes. It was found that the oil yield from seeds of *Meconopsis Wallichii* grown at Darjeeling is fairly high, being about 44 per cent. of the seed weight. A comparison of the oil constants with those of common poppy seed oil is summarised on p. 141.

The acid values of vegetable oils are generally high. This is also in evidence in the case of the different species of Meconopsis and *Papaver somniferum.* In the present instances the most notable fact is the high R.M. value (soluble volatile fatty acid) in the oil of *Meconopsis Walli-*

chii, which points to its being a good edible oil, as in the case of butter fats.

The least iodine value is that of *Meconopsis paniculata* acid mixture. This is probably interpretable by the absence of linolenic acid in the mixture, as evidenced by there being no hexa-bromide formed when brominated.

From considerations of the drying quality of the oils as compared with poppy seed oil, it is to be expected that in some cases, where the yield is sufficiently high, as in the case of Darjeeling-grown *Meconopsis Wallichii*, these oils may perhaps prove of some economic importance.

We take this opportunity of expressing our grateful thanks to Sir J. C. Bose for constant encouragement and facilities given us for this investigation.

Sample	Oil yield per cent	Specific gravity	Coefficient of expansion	Refractive Index
Papaver somniferum (Lewkowitsch)	41·0	0·9240 at 15° C.	—	1·4586 at 60° C.
P. somniferum (Leather)	48·6	0·9270 at 15° C.	—	1·4772 at 15° C.
Meconopsis napaulensis	26·22	0·9180 at 30° C.	0·000612 (30°–90° C.)	1·4731 at 30° C.
M. paniculata	32·5	0·9212 at 26° C.	0·000630 (26°–98° C.)	1·4735 at 32° C.
M. Wallichii (Tonglu and Higher Alt.)	34·2	0·93205 at 28° C.	0·000716 (28°–100° C.)	1·4753 at 28° C.
M. Wallichii (Darjeeling)	43·95	—	—	—

Sample	Saponification value	Unsaponifiable matter	Iodine value of oil	Acid value	R.M. value
Papaver somniferum (foreign)	195	0·43	133–144	0·7–11	0·00
P. somniferum (Indian)	189–196	—	132–157	—	0·00
Meconopsis napaulensis	181–187	0·62	130·3	40·6	0·21
M. paniculata	187	1·06	125·2	32·0	—
M. Wallichii	182·2	0·91	128·7	14·2	8·32

Sample	Per cent. of free fatty acid insoluble in water	Iodine value	Refractive Index	Neutralisation value	Mean mol. wt.
Papaver somniferum	95·2	139	1·4506 at 60° C.	199	281
Meconopsis napaulensis	95·1	135	1·4633 at 31° C.	191	293
M. paniculata	95·4	128	1·4643 at 32° C.	—	—
M. Wallichii	94·88	132·7	0·4715 at 25° C.	—	—

SOLID ACID PORTION

Sample	Per cent. yield	Iodine value	Melting point	Solidifying point
Meconopsis napaulensis .	23·90	37·50	45° C.	43° C.
M. paniculata .	18·89	10·58	51° C.	49° C.
M. Wallichii .	12·00	12·07	48° C.	46° C.

The values for *Papaver somniferum* are not given in Lewkowitsch.

LIQUID ACID PORTION

Sample	Yield per cent.	Iodine value	Refractive Index	Oleic acid per cent.	Linolic acid per cent.	Linolenic acid per cent.
Papaver somniferum	—	149·6	—	—	—	—
Meconopsis napaulensis	76·10	140·0	1·4678 at 31° C.	34·03	61·60	2·78
M. paniculata .	81·11	151·13	1·4678 at 30° C.	25·50	70·00	0·00
M. Wallichii	88·00	145·96	1·4715 at 26° C.	33·92	61·18	1·75

IX.—CHEMICAL AND PHYSIOLOGICAL INVESTIGATIONS ON PRESENCE OF VITAMIN C IN CERTAIN SUBSTANCES IN PLANTS

BY

H. N. BANERJEE, M.Sc.

THERE has recently been rapid progress in the quick detection and estimation of Vitamin C (Ascorbic Acid) in plant and animal products. This has been rendered possible by the development of chemical methods for the quantitative estimation according to the modified Tillmans technique[1] of titration with 2 : 6 dichlorophenol-indophenol, the oxidation reduction indicator. The present investigation was undertaken to utilise this quick method of determination in order to make a general survey of the Ascorbic Acid content in Indian food stuffs as well as to find a rich source of this particular vitamin.

The juice of Date Palm, of Palmyra Palm and of Cocoanut Palm is drunk in Calcutta during the winter season ; it is also imbibed as *toddy* or fermented juice during the whole year. As regards the juice of the Cocoanut it can be obtained from the spadix, as in the case of the Palmyra Palm. The juices were procured for our investigation from Dhakuria, a suburb of Calcutta.

As a rule the juice was collected during the whole night in earthen pots which had been sterilised by smoking.

The following investigations were undertaken :

1. Chemical estimation of Ascorbic Acid in Date Palm juice and its product (*Gur*), in Cocoanut Palm juice and in Palmyra Palm juice.
2. Stability of Ascorbic Acid in the above juices and the absence of interfering substances.

[1] Birch, Harris and Ray, *Biochem. J.*, vol. xxvii, pp. 580. 590.

3. Presence of Ascorbic Acid synthesising substance in the juices.
4. Urinary excretion of Ascorbic Acid after feeding with mannose.
5. Ascorbic Acid in Cocoanut water and kernel. Chemical and physiological assay.
6. Variation in the quantity of Ascorbic Acid in different parts of Cocoanut with age, and the rôle of Ascorbic Acid in germination.
7. Ascorbic Acid destroying agent in Cocoanut fibre.
8. Comparative instability of Ascorbic Acid in *Citrus decumana*.

Examination of Juice from the Date Palm

I first describe the results of examination of the juice from Date Palm. For this, samples from the collecting pots, each from a different tree, were brought to the laboratory in the morning in glass-stoppered bottles and titrated against a freshly prepared standardised solution of the indicator. The indicator was titrated against pure Ascorbic

Table I.—Results of Examination of Juice from Date Palm

Sample No.	Natural *p*H of the juice	Milligrams of Ascorbic Acid in 10 c.c. juice
1	4·6	1·08
2	4·4	0·84
3	4·5	1·10
4	4·2	0·40
5	4·2	1·20
6	4·2	0·80
7	5·0	1·40
8	5·0	1·90
9	5·4	3·40
10	5·1	1·60
11	5·6	0·80
12	6·3	0·80
13	4·9	1·60
14	4·9	1·50

Acid solution, which again in its turn was tested by standard iodine solution. In each case the juice was adjusted to $pH = 3$, by adding the requisite amount of glacial acetic acid before titration. Each c.c. of the indicator solution was equivalent to 1 mg. of Ascorbic Acid.[1]

The results are tabulated in Table I, in which the last column represents the amount in c.c. of the indicator used, which is also the amount in mgs. of Ascorbic Acid in 10 c.c. juice.

It will be seen from the above results that Date Palm juice is a rich source of Ascorbic Acid. The juice is generally boiled down to syrupy consistency, called *Poira Gur*, or boiled down to dry cake, called *Patali Gur*. I next undertook to examine different samples of these collected from various localities, and also samples prepared from day to day under our own supervision at the Falta Field Station. I give below the results obtained.

TABLE IA.—RESULTS OF EXAMINATION OF *POIRA GUR*

Sample No.	Percentage of moisture	Milligrams of Ascorbic Acid per gram of *Poira Gur*	Locality
1	18·0	2·00	Nadia
2	20·5	1·80	Falta Field St.
3	20·6	0·96	
4	23·0	1·00	
5	29·0	0·90	,, ,, ,,
6	29·2	1·60	,, ,, ,,
7	31·8	1·50	,, ,, ,,
	33·0	1·00	,, ,, ,,
9	34·0	0·54	Local Market
10	40·1	0·80	Falta Field St.
11	41·5	0·70	

The most important fact in the above results is that boiling down the juice did not destroy the Ascorbic Acid. Indeed some of the samples contained 2 mgs. of Ascorbic Acid per gram of the *Gur*, which is a very high value.

[1] H. N. Banerjee, *Current Science*, vol. iv, pp. 28–9.

TABLE Ib.—RESULTS OF EXAMINATION OF *PATALI GUR*

Sample No.	Milligrams of Ascorbic Acid per gram of *Patali Gur*
1	0·60
2	0·48
3	0·88
4	0·75
5	0·95
6	1·50
7	2·00

Generally speaking, *Patali Gur* contains less Ascorbic Acid than *Poira Gur*, weight for weight, although the latter is liquid and contains a higher percentage of water.

It may be remarked in passing that sugar-cane juice obtained from Calcutta market gave very poor Ascorbic Acid content. Sugar-cane *Gur* also did not show the presence of any appreciable quantity of Vitamin C. *Gur* from Palmyra Palm juice, of which more than a dozen samples from different localities were examined, showed the presence of Ascorbic Acid, which varied from 0·25 mg. to 0·55 mg. per gram of the *Gur cake*.

EXAMINATION OF JUICE OF PALMYRA PALM

The following are the results obtained from two typical samples :

TABLE II.—JUICE FROM PALMYRA PALM

Sample No.	Natural *p*H	Milligrams of Ascorbic Acid in 10 c.c. juice
1	4·8	1·90
2	4·4	0·80

The occurence of Ascorbic Acid in animal tissues has been observed by many workers,[1] and the presence of this

[1] Bourne and Allen, *Nature*, vol. 136, p. 185. Tauber and Kleiner, *Biochem. J.*, vol. xxviii, pp. 268, 1154.

substance has been regarded as of essential importance for the respiration of the tissues. The presence of Ascorbic Acid in plant fluids, as described above, may, therefore, prove to be of considerable significance.

Examination of Juice of Cocoanut Palm

The results of examination of Cocoanut juice are summarised as follows :

Table III.—Results of Examination of Juice from Cocoanut Palm

Sample No.	Natural *p*H of juice	Milligrams of Ascorbic Acid in 10 c.c. juice
1	4·7	1·60
2	4·6	1·60
3	4·7	1·80
4	4·5	2·00
5	4·6	1·60
6	4·6	1·60
7	4·6	3·00
8	4·5	3·00
9	4·4	1·60
10	4·5	2·60
11	4·7	1·80
12	4·6	1·20
13	4·4	1·60
14	4·5	1·20

The *p*H values of the different samples of Cocoanut Palm juice lie within very narrow limits—4·4 to 4·7.

Absence of Interfering Foreign Substances

The estimations which have been described were all carried out in acid solutions, as Birch, Harris and Ray have shown that certain naturally occurring reducing agents, notably Glutathione and certain phenolic compounds, tend to reduce the indicator in neutral and alkaline solutions. Under the above condition it is claimed that there is proportionality between the antiscorbutic activity of the substances and Tillman's reduction value as expressed here.

Emmerie [1] maintains that Cysteine, etc., may vitiate the results even in acid solution. All the above experiments were therefore repeated with juice treated according to Emmerie's modification : precipitation by mercuric acetate followed by treatment with H_2S, and final removal of the H_2S by CO_2, controlled by lead acetate paper and also nitroprusside reactions. Even after these treatments the titration value did not show any difference. It is thus evident that there is no interfering substance in the above juices.

Stability of Ascorbic Acid in the Juices

Plant juices are liable to undergo fermentation, and it would not be surprising if the Ascorbic Acid content were to suffer change. To investigate this point the juices were exposed to the atmosphere at laboratory temperature for a period of 24 hours, during which period there was abundant evidence of fermentation with brisk evolution of CO_2. After 24 hours the juices were examined and the following results were obtained :

Table IV.—Comparative Statement of the Presence of Ascorbic Acid before and after Fermentation

	Milligrams of Ascorbic Acid in 10 c.c. juice to start with	Milligrams of Ascorbic Acid in 10 c.c. juice after 24 hours
Date Palm 1	1·60	1·60
,, ,, 2	1·50	1·50
Cocoanut Palm 1	1·60	1·60
,, ,, 2	2·60	2·60
,, ,, 3	1·80	1·80
,, ,, 4	1·20	1·20
,, ,, 5	1·20	1·20
Palmyra Palm 1	1·90	1·90
,, ,, 2	1·85	1·85

[1] A. Emmerie and M. V. Ekelen, *Biochem. J.*, vol. xxviii (1934), p. 1154.

From the above it will be evident that there was no difference in the values between the results in the beginning and after 24 hours. Fermentation and exposure to atmosphere seem to have no effect upon the Ascorbic Acid content of the juices from the three palms.

The presence of Ascorbic Acid along with sugars in the juices suggests the possibility of synthesising enzymes in the plant which can convert the sugars under suitable conditions into Vitamin C. Ray[1] suggests the possibility of the presence of such an enzyme in pea seedlings. My own experiments with plant fluids have also led me to a somewhat similar conclusion.

In order to test this question whether the juices can synthesise Ascorbic Acid from the sugars, the following experiments were carried out by adding to the sugars plant juices at definite incubation temperatures as detailed below.

Incubation Experiments

Several sterilised glass-stoppered bottles filled with freshly collected plant fluids (50 c.c. in each bottle) with the addition of 0·5 gram of different sugars were placed for 12 hours in an incubator at 37° C. to 39° C., this temperature range being most favourable for enzyme reactions. Five c.c. of the fluid from each bottle were then drawn out and severally examined. Control experiments were also carried out with 5 c.c. of incubated plant fluids without addition of any sugars. Emmerie's method was followed in every case. The results are tabulated in every case.

It may be stated here that further prolongation of the period of incubation did not produce any additional change. The increase in the titre for the incubated solution after treatment by Emmerie's method shows that a considerable amount of Ascorbic Acid remains in the reversibly oxidised state.

The results indicate that there are some substances present in the plant juice which are capable of synthesising Ascorbic Acid from some of the sugars. Sucrose, however, is not at all affected.

[1] S. N. Ray, *Biochem. J.*, vol. xxviii, p. 999.

TABLE V.—RESULTS OF INCUBATION EXPERIMENTS

Titre for 5 c.c. at commencement		Titre for 5 c.c. after 12 hours	Titre for 5. c.c. by Emmerie treatment
Date Palm Juice (natural *p*H = 5·6)			
50 c.c. juice as control	0·65	0·65	0·78
,, ,, with 0·5 gram mannose		0·82	0·93
,, ,, ,, glucose		0·80	0·92
,, ,, ,, fructose		0·80	0·90
,, ,, ,, lactose		0·78	0·82
,, ,, ,, sucrose		0·65	0·78
Cocoanut Palm Juice (natural *p*H = 4·6)			
50 c.c. juice as control	0·25	0·25	0·30
,, ,, with 0·5 gram mannose		0·40	0·50
,, ,, ,, glucose		0·35	0·40
,, ,, ,, fructose		0·35	0·40
,, ,, ,, lactose		0·30	0·35
,, ,, ,, sucrose		0·25	0·30
Palmyra Palm Juice (natural *p*H = 4·6)			
50 c.c. juice as control	0·35	0·35	0·45
,, ,, with 0·5 gram mannose		0·45	0·56

Note.—In regard to the results described above my attention has recently been drawn to the work of A. G. Jonnissian (*Proc. 6th Caucasus Cong. Physiol. Pharmaco. and Biochem.*, Acad. Sc. Press, Mocsow and Leningrad, 101, 1935), which casts doubt on the applicability of Tillman's reagent in presence of fructose and arabinose. The results of my experiments with glucose and other sugars, however, prove that the doubt is not justifiable. This conclusion is also supported by A. L. Bacharach and H. E. Glynn (*Nature*, vol. 136 (1935), p. 757.

MANNOSE AS A PRECURSOR OF VITAMIN C

Guha and Ghose [1] have recently observed that isolated kidney, liver and spleen of rats in Ringer solution can

[1] Guha and Ghose, *Nature*, vol. 134 (1934), p. 739; vol. 135 (1935), p. 871.

convert mannose into Vitamin C. They have further found, by conducting the experiments *in vivo* by injecting mannose and other sugars into rats, that the Ascorbic Acid content of tissues undergoes a rapid increase.

The observations detailed below were undertaken with a view to investigate how far there was a correspondence, in synthesising Ascorbic Acid from carbohydrates in the metabolism of plants and animals. Römer *et al*[1] report that, like rats and birds, human infants have the power of synthesising Vitamin C, and that this property is maximum at an age of nearly five months, diminishing ultimately and disappearing altogether after 14 months. Geoffrey Bourne [2] found that luteal tissue is capable of synthesising Vitamin C. He suggests that the synthesis of Vitamin C takes place first in the *corpus luteum*, and after the fœtus was developed it either takes over or supplements the vitaminogenic function of the luteal tissue. That a similar function may also exist in the lower organism is indicated in the works of Bourne and Allen.[3]

Reference has already been made of observations showing that mannose was readily converted into Vitamin C by rats and seedlings. I undertook investigations on the effect of mannose on a human child, a boy five months old and entirely breast fed. For the first five days the normal urine of the child, passed between the hours of 5 and 11 A.M. daily, was collected over sulphuric acid (as many drops of concentrated acid as the number of c.c. of urine collected) and the Ascorbic Acid content determined by the usual titrimetric method of assay. The morning urine only was tested, following the experience of Johnson and Zilva.[4] The level of vitamin excretion for this period of five days was found to be practically constant. After this the child was given a daily dose of one gram of mannose dissolved in the mother's milk at 7 P.M. From the next morning it was observed that the Ascorbic Acid excretion began to increase considerably, continuing to do so during the whole period of mannose feeding for a week.

After the above one week period of mannose feeding, when the Vitamin C content showed a considerable rise, the

[1] Römer *et al*, *Nature*, vol. 134 (1934), p. 142.
[2] Geoffrey Bourne, *Nature*, vol. 135 (1935), pp. 148–49.
[3] Bourne and Allen, *Nature*, vol. 135 (1935), p. 185.
[4] Johnson and Zilva, *Biochem. J.*, vol. xxviii, p. 1393.

stoppage of mannose was followed by immediate fall to about the original normal level.

The following is a tabular statement of the results of examination under different conditions :

TABLE VIA.—PRE-MANNOSE PERIOD

Dates of observation	Milligrams of Ascorbic Acid in 10 c.c. urine
17/1/35	0·15
18/1/35	0·10
19/1/35	0·20
20/1/35	0·11
20/1/35	0·18

TABLE VIB.—MANNOSE FEEDING PERIOD

Dates	Milligrams of Ascorbic Acid in 10 c.c. urine
22/1/35	0·45
23/1/35	0·54
24/1/35	0·36
25/1/35	0·36
26/1/35	0·32
27/1/35	0·50

TABLE VIC.—AFTER STOPPAGE OF MANNOSE

Dates	Milligrams of Ascorbic Acid in 10 c.c. urine
28/1/35	0·28
29/1/35	0·11
30/1/35	0·22
31/1/35	0·12
1/2/35	0·15
2/2/35	0·12

N.B.—Some of the results detailed above were published in a preliminary note to *Current Science*, vol. iii, No. 8, pp. 355–6.

The above results graphically represented below clearly indicate the conversion of mannose into Vitamin C (fig. 55).

In repeating the investigation with an older child aged 3 years it was, however, found that Ascorbic Acid concentration in the urine did not exhibit any change. This proves that in the efficiency for conversion of mannose into Ascorbic

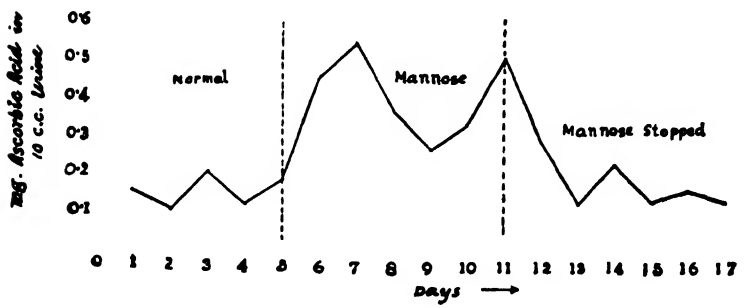

FIG. 55. Conversion of Mannose into Ascorbic Acid.

Acid, a certain low limit in the age of the child must not be exceeded. It must be mentioned, however, that the volume of urine collected between the hours of 5 and 11 A.M., in the case of the older child, increased considerably, whereas in the case of the younger subject the quantity of urine remained practically constant.

COCOANUT FRUIT CONTENTS—KERNEL AND WATER

As it was found in the course of the experiments that have already been described that the Cocoanut Palm juice was very rich in Vitamin C, the edible contents of the fruit were next taken up for investigation.

Vitamin content in both the kernel and water was determined by the titrimetric method and also tested physiologically by its reaction on guinea pigs.

BIOLOGICAL EXPERIMENTS

The biological experiments were carried out by the protective technique. For this, guinea pigs weighing

between 200 and 300 grams each were housed in experimental cages and fed for a week with the following basal rations :

70 parts oatmeal
20 parts crushed gram (*Chhola*)
10 parts bran
1 part cod liver oil, and
a certain quantity of green vegetables.

Salt was also supplied by placing a block of rock salt in each cage.

The experimental observations are as follows :

1. Effect of supply of basal diet alone (without green vegetables), this being regarded as the control experiment.
2. Effect of basal diet with addition of green vegetables, this being regarded as the protective diet.
3. Replacement of green food in (2) and adding cocoanut water in each case.
4. Replacement of green food in (2) and adding cocoanut kernel in each case.

Experiment 1. In this, it is to be remembered, there was supply of basal diet without green vegetables. The experimental guinea pigs underwent a rapid decline in weight and died in the course of four weeks, showing signs of scurvy.

TABLE VII.—PHYSIOLOGICAL EFFECT OF BASAL DIET ALONE

Guinea pig	Weight in grams						
	June		July				
	18th	25th	1st	8th	11th	15th	18th
No. 1	225	235	215	180	Died at 170	—	—
No. 2	190	201	220	205	175	Died at 155	
No. 3	220	214	225	222	180	180	Died at 180

The results prove that the basal diet alone could not protect life and continued growth.

Experiment 2. Under this protective diet, that is, basal diet with the addition of green vegetables, the guinea pigs showed normal growth with increase of weight.

Experiment 3. In this the cocoanut water took the place of green vegetables. In such cases the growth and health of the animals were maintained normal The results, in Table VIII, prove that cocoanut water supplies the necessary vitamin.

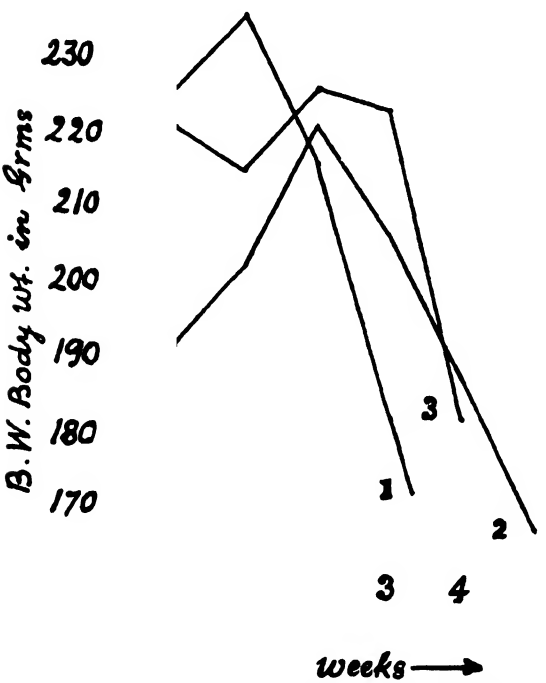

FIG. 56. Effect of Basal Diet alone. All the Guinea Pigs died of Scurvy.

Experiment 4. In this case cocoanut kernel took the place of cocoanut water. Here also the guinea pigs maintained their normal health and growth. The results are summarised in Table IX.

The results detailed in Tables VIII and IX are graphically represented in figs. 56 and 57.

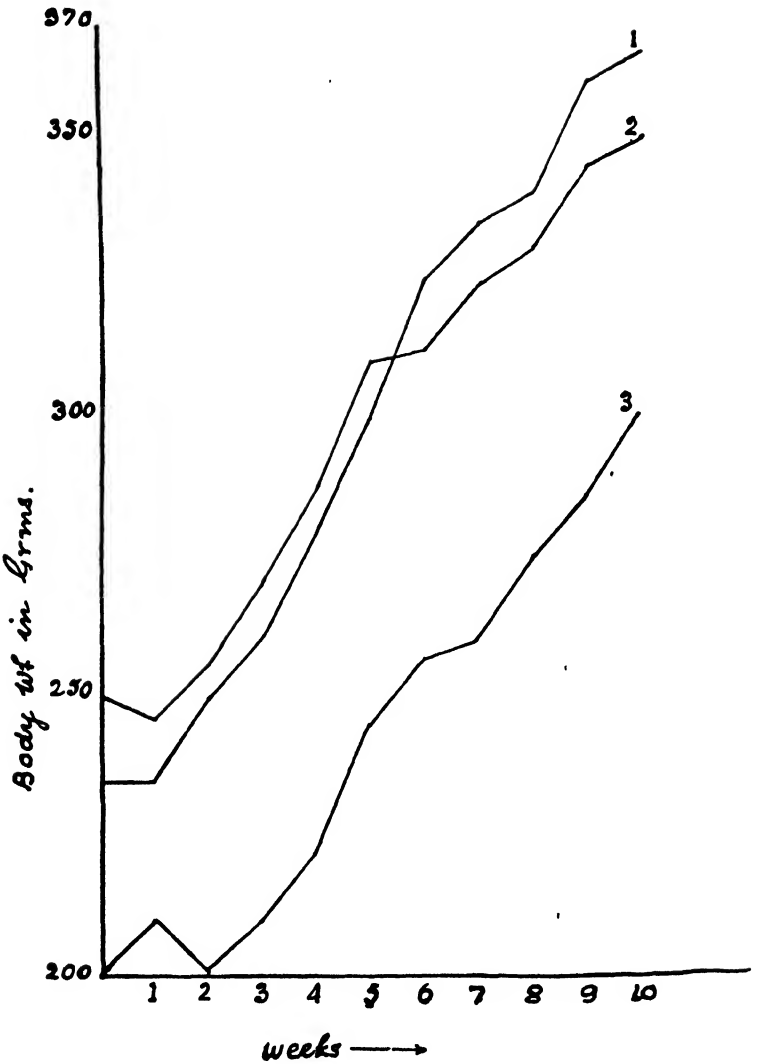

FIG. 57. Curves 1 and 2 for Guinea Pigs on Cocoanut Water
Curve 3 for Guinea Pigs on Cocoanut Kernel.

The physiological experiments were also supplemented by chemical examination.

TABLE VIII.—BASAL DIET AND 20 C.C. COCOANUT WATER
(Minimum Protective Dose)

Guinea pig	Weight in grams												
	June		July								August		
	16th	23rd	1st	4th	8th	11th	15th	18th	23rd	29th	5th	12th	26th
No. 1	235	235	250	255	261	270	280	290	300	325	335	340	365
No. 2	250	246	256	261	271	280	288	295	310	312	324	330	350

TABLE IX.—BASAL DIET AND 10 GRAMS COCOANUT KERNEL
(Minimum Protective Dose)

Guinea pig	Weight in grams												
	June		July								August		
	16th	23rd	1st	4th	8th	11th	15th	18th	23rd	29th	5th	12th	26th
No. 1	201	210	200	206	210	214	222	230	245	257	260	275	300

CHEMICAL ASSAY OF COCOANUT WATER AND KERNEL FOR ASCORBIC ACID

For this purpose fresh fruits were subjected to examination. The water of the fruit was adjusted to pH = 3 in each case by the addition of glacial acetic acid, and titrated against the standard indicator.

In the case of kernel, this was crushed with clean sand in a porcelain pestle and mortar and extracted first with a 10 per cent. solution of trichloro-acetic acid and then twice with 5 per cent., with the precaution that in no case the liquid so extracted contained more than 3 per cent. of trichloro-acetic acid.[1]

The titration results are given below, the fruits being of different stages of maturity, (*a*) green and (*b*) fully ripe.

[1] McHenry and Graham, *Biochem. J.*, vol. xxix, p. 2013. B. Ahmed, *Biochem. J.*, vol. xxix, p. 275.

TABLE XA.—ASCORBIC ACID CONTENT IN GREEN COCOANUT

Fruit No.	Volume of water in c.c.	Natural *p*H of water	Milligrams of Ascorbic Acid in	
			10 c.c. water	10 grams kernel
1	400	5·1	0·20	0·36
2	270	5·6	0·19	0·19
3	430	5·3	0·19	0·30
4	185	5·2	0·12	0·16
5	345	4·8	0·28	0·28
6	330	5·0	0·18	0·28

TABLE XB.—ASCORBIC ACID CONTENT IN RIPE COCOANUT

Fruit No.	Volume of water in c c.	Natural *p*H of water	Milligrams of Ascorbic Acid in	
			10 c.c. water	10 grams kernel
1	58	6·1	0·12	0·275
2	65	6·0	0·22	0·357
3	160	6·2	0·21	0·200
4	220	5·9	0·28	0·275
5	222	5·3	0·20	0·270
6	275	5·3	0·15	0·330

The titre value of cocoanut water and of the extract from kernel did not suffer any variation by boiling with water or with trichloro-acetic acid.

Reference may be made to the works of McHenry and Graham [1] and of B. Ahmed, who obtained discordant results while working with cabbage and other substances.

STABILITY OF VITAMIN C IN COCOANUT WATER

Vitamin C, generally speaking, in natural sources is liable to easy oxidation and deterioration by exposure to air. A solution of pure Ascorbic Acid rapidly deteriorates by heat or by aeration,[2] and this is enhanced by minute traces of mineral matter.[3] But the water of cocoanut was

[1] McHenry and Graham, *Nature*, vol. 135 (1935), p. 871.
[2] Birch, Harris and Ray, *Biochem. J.*, vol. xxvii, p. 580.
[3] Kellie and Zilva, *Biochem. J.*, vol. xxix, p. 1028.

found to be stable in this respect; boiled briskly for 30 minutes the titre did not suffer any variation. On aeration continually for one and a half hours there was loss of only 8·3 per cent. On standing for spontaneous fermentation which occurs after much longer periods, it was found that there was no variation in the Ascorbic Acid content even after 24 hours.

The following tables exhibit the stability of Ascorbic Acid in cocoanut water under different conditions of treatment:

TABLE XI.—STABILITY TO BOILING OF COCOANUT WATER

Fresh Ripe Fruit. Total volume of water 125 c.c. pH = 5·2.

Duration of boiling	Titre for 10 c.c. of water
0 minutes	0·25
10 ,,	0·25
30 ,,	0·25

TABLE XII.—STABILITY TO AERATION OF COCOANUT WATER

Duration of aeration	Titre for 10 c c of water
0 minutes	0·24
30 ,,	0·24
60 ,,	0·24
90 ,,	0·22

TABLE XIII.—STABILITY DURING FERMENTATION OF COCOANUT WATER

Duration of fermentation	Titre for 10 c.c. of water
0 hours	0·25
24 ,,	0·25

In the experiments described it is evident that neither boiling alone, nor aeration by itself, nor fermentation has

any pronounced effect upon the Ascorbic Acid content of cocoanut water. In this connection it should be mentioned that aeration of cocoanut water for ten minutes after *previous boiling* for 15 minutes was found completely to destroy the Vitamin C. This would indicate that there is present in the cocoanut water a thermo-labile protective substance which probably acts against aerobic oxidation. In all these experiments the precaution was taken to use double-distilled water, the vessels used being always Jena glass.

The question of stability of Vitamin C in cocoanut kernel under desiccation and exposure to air was now investigated. In regard to dessication over sulphuric acid in an ordinary desiccator for 24 hours, the loss in Ascorbic Acid was only 3 per cent., whereas the actual loss in weight of the kernel substance was 20 per cent. The results of the experiment are given in Table XIV.

TABLE XIV.—STABILITY OF ASCORBIC ACID IN COCOANUT KERNEL UNDER DESICCATION AND EXPOSURE TO AIR

Duration of desiccation and exposure to Air	Titre for 20 grams of kernel	Loss of weight due to desiccation per cent.	Loss of potency per cent.
0 hours	0·66	—	—
24 ,,	0·64	20	3·0
48 ,,	0·52	45	20·9
72 ,,	0·36	50	45·4

The object of the next investigation was the study of the effect of age on the amount of Ascorbic Acid in the water and in the kernel.

EFFECT OF AGE ON THE CONCENTRATION OF ASCORBIC ACID IN WATER AND IN KERNEL

While examining the Ascorbic Acid content of water and kernel of cocoanut fruit of different ages, certain interesting facts were observed, such as the transference of Ascorbic Acid from the water to the kernel with increasing maturity of the fruit. It was found that with increasing

age up to a certain limit the Ascorbic Acid content in the water and in the kernel undergoes an increase. But after the fruit on the tree has become ripened the Ascorbic Acid in the water begins to decrease while that in the kernel undergoes an increase. Afterwards, as the fruit further ripens, the quantity of kernel increases as also its Ascorbic Acid concentration, whereas that in the water practically disappears in a fully ripe and dry fruit. In this latter case the kernel is very rich in Ascorbic Acid even to the point of advanced germination. The actual results are tabulated below:

TABLE XV.—EFFECT OF AGE ON VARIATION OF ASCORBIC ACID IN COCOANUT WATER AND KERNEL

Description of the fruit	Milligrams of Ascorbic Acid in 10 c.c. water	Milligrams of Ascorbic Acid in 10 grams kernel
Immature fruit *without* kernel .	0·133	—
Fruit with very soft kernel .	0·190	0·160
Mature fruit with soft kernel .	0·220	0·225
Fresh ripe fruit with hard kernel	0·200	0·360
Dry fruit with follicle . .	0·030	0·275

The results tabulated above show that there is a gradual transference of Ascorbic Acid from the water to the kernel as the fruit ripens. By the time the follicle begins to form the Ascorbic Acid of the kernel begins apparently to become transferred to the follicle.

After the attainment of this stage the question of transference of Ascorbic Acid from the kernel to the growing embryo was investigated. It is to be remembered that the inside follicle has been formed *within the shell* of the fruit, while the *embryo* is now protruding outside the shell. The water, as previously explained, is at this stage practically free of Ascorbic Acid; this acid is contained in the kernel and is gradually being transferred via the follicle to the embryo. The progress of this transference will be clear from the results obtained with typical samples as summarised in Table XVI.

TABLE XVI.—TRANSFERENCE OF ASCORBIC ACID FROM THE KERNEL TO THE FOLLICLE AND THE EMBRYO

Fruit sample No.	Volume of water	Milligrams of Ascorbic Acid			
		Water	Kernel	In fol	Embryo outside
1	40 c.c.	Nil	0·018	0·	0·090
2	50 c.c.	Nil	0·015	0·	0·105
3	135 c.c.	Nil	0·020	0·	0·300
4	60 c.c.	Nil	0·020	0·260	0·340
5	75 c.c.	Nil	0·026	0·110	0·300
6	25 c.c.	Nil	0·030	0·100	0·150
7	80 c.c.	Nil	0·040	0·100	0·400
8	60 c.c.	Nil	0·066	0·188	0·400

The results show that the Ascorbic Acid in the embryo is gradually increased ; the presence of increasing quantities is associated with its growth.

GROWTH OF ISOLATED EMBRYO

If the supply of Ascorbic Acid is essential for growth of the embryo, a similar result may be secured by supplying the acid to an isolated embryo. The investigation on this subject was carried out as follows. Two similar specimens, one the experimental and the other the control, were taken, having the same weight of 1 gram. Both of them were placed in the sterile culture medium (Knopp solution). The experimental specimen alone was supplied with Ascorbic Acid of strength one in ten thousand. After a week the dry weights of the two specimens were obtained. It was found that while the control weighed only 1·1 gram, the experimental specimen had attained the very much larger weight of 2·4 grams. This affords a very definite proof of the efficacy of Ascorbic Acid on growth of embryo.

Recently Hausen[1] has reported that 'Torstai' peas grown on sterile Hiltner solution with addition of Ascorbic Acid showed enhanced growth in comparison with the

[1] Synnove Hausen, *Soumen Kemistilehti B*, 5–6 (1935), and *Nature*, vol. 136 (1935), p. 516.

control grown on the medium alone. These results have also been confirmed by Havas.[1] My observation, with germinating cocoanut, points to the same conclusion.

Action of Fibre on Cocoanut Water

In the course of these investigations a very curious phenomenon was observed that the water in some of the cocoanut fruits, which usually contain large quantities of Ascorbic Acid, was totally devoid of it. This characteristic effect was finally traced to the fact that there were cracks in the fruit shell through which the water came in contact with fibres. It was hence surmised that the fibres probably contained something which destroyed the Ascorbic Acid. To verify this suggestion certain experiments were carried out, the results of which are tabulated below :

Water from a mature green cocoanut fruit was placed into 4 bottles.

No. 1 bottle contained fruit water only as control.

No. 2 bottle contained fruit water + 10 grams fibre of the same fruit.

No. 3 bottle contained 20 c.c. fruit water + 10 c.c. juice pressed out from the fibres.

No. 4 bottle contained 20 c.c. fruit water + 10 c.c. aqueous extract from 20 grams of fibre.

For purposes of comparison, 15 c.c. of the solutions in bottles Nos. 3 and 4 correspond to 10 c.c. of the cocoanut water.

The results are given in Table XVII, it being understood that 10 c.c. of cocoanut water was equivalent to 0·11 c.c. Standard Indicator. The observation, started at 8 A.M., was repeated at intervals of 4 hours, namely, at 12 noon and 4 P.M.

Table XVII.—Action of Fibre on the Cocoanut Water

Time of observation	Titre for 10 c.c. No. 1	Titre for 10 c.c. No. 2	Titre for 15 c.c. No. 3	Titre for 15 c.c. No. 4
12 noon	0·11	0·06	0·03	0·03
4 P.M.	0·11	0·03	0·00	0·00

[1] Laszlo Havas, *Nature*, vol. 136 (1935), p. 435.

It will be seen from the results given in columns 2, 3 and 4 that fibres or their extracts partially or wholly destroy the Ascorbic Acid.

The experiment was next repeated with the modification that the cocoanut water was taken from a ripe fruit while the fibre was taken from a green cocoanut. The notations used are the same as in the previous case. The results are tabulated below. It is to be remembered that the Ascorbic Acid concentration in the water of the ripe fruit, for every 10 c.c., was equivalent to 0·16 c.c. of the Standard Indicator.

TABLE XVIII.—ACTION OF GREEN FIBRE ON WATER FROM A RIPE FRUIT

Time of observation	Titre for 10 c.c. No. 1	Titre for 10 c.c. No. 2	Titre for 15 c.c. No. 3	Titre for 15 c.c. No. 4
12 noon	0·16	0·09	0·06	0·06
4 P.M.	0·16	0·03	0·03	0·03

In this particular experiment on the effect of green fibres on cocoanut water, we find that the fibres tend to destroy the Ascorbic Acid.

Further experiments were carried out in solutions of Ascorbic Acid only in distilled water, in which fibres from green cocoanut were introduced. In such cases the Ascorbic Acid in the solutions was found to undergo destruction in the course of about 5 hours.

The results of the various experiments that have been described indicate that the fibres from green cocoanut fruit contain some water-soluble substance which destroys the Ascorbic Acid. It explains the observed fact that in some of the green cocoanut fruits no Ascorbic Acid could be detected, since through the cracks in the shell the green fibres or the soluble disturbing factor had come in contact with the water inside.

It is interesting to note in this connection that an enzyme has recently been discovered in the pericarp of Hubbarb Squash[1] which has the power of destroying Ascorbic Acid

[1] H. Tauber, I. S. Kleiner and G. Miski, *Biochem. J.*, vol. cx, p. 211.

by oxidation. A similar result has also been observed in regard to Drumstick.[1]

Having described the variation of Ascorbic Acid content in the cocoanut induced under different conditions, I shall proceed to describe the decomposition of Ascorbic Acid in another fruit, *Citrus decumana*.

The Decomposition of Ascorbic Acid in *Citrus decumana*

This is an edible fruit known in Bengal as *Batabi-Nebu*. The method of examination is given below.

The juice from the fruit (excluding the rind) was pressed out through cloth of fine texture and titrated against a Standard Indicator. The residue left over was then extracted with trichloro-acetic acid in the usual manner as previously described. The extract thus obtained from the residue was separately titrated. From these two determinations the total Ascorbic Acid content in the material was calculated. In cases where the juices were pink, the colour was discharged by dilution with extra pure distilled water. The result of estimation with a typical specimen is given below.

Table XIX.—Ascorbic Acid in the Juice from *Citrus decumana*

Fruit material	Volume of juice	Natural *p*H	Titre for 10 c.c. juice	Milligrams of Ascorbic Acid per gram of material
50 grams	36 c.c.	3·9	7·4 c.c.	0·54

Having determined the quantitative value of total Ascorbic Acid in the material, I investigated the effect of (*a*) Exposure to air, of (*b*) Boiling and of (*c*) Enforced Aeration on the decomposition of the Ascorbic Acid present in the solution of the expressed juice. The juice was diluted ten times by adding a sufficient quantity of distilled water.

[1] M. Srinivasan, *Current Science*, vol. iv, p. 407.

(a) *Effect of Exposure of the Juice Solution to Air*

	At the commencement	After 30 minutes	After 60 minutes	After 120 minutes	After 240 minutes
tre for 5 c.c. of solution .	0·37	0·35	0·33	0·32	0·29
ɔss per cent.	—	5·4	10·8	13·5	21·7

(b) *Effect of Boiling of the Juice Solution*

	At the commencement	After 5 minutes	After 10 minutes
Titre for 5 c.c. of solution . .	0·37	0·30	0·00
Loss per cent. .	—	19	100

(c) *Effect of Enforced Aeration of the Juice Solution*

	At the commencement	After 10 minutes	After 30 minutes	After 6 minute	
Titre for 5 c.c. of solution .	0·37	0·35	0·34	0·31	
Loss per cent.	—	5·4	8·1	16·2	32·4

It will be seen from the results given in the tables that juice expressed from *Citrus decumana* is subject to deterioration even after simple exposure to air, that this destruction

is more rapid consequent on enforced aeration, and is complete after boiling.

In this connection it may be mentioned that Harris and Ray found that there is a loss of 6 per cent. in the Ascorbic Acid content of orange juice in the course of aeration for 40 minutes. Reference may also be made to B. Ahmed's results with shredded *Kerala*, which loses 70 per cent. of its Ascorbic Acid content on simple exposure to air. Kohman *et al* report similar destruction in the case of carrots.

Mawson [1] is of opinion, from his work on the influence of animal tissues on the oxidation of Ascorbic Acid, that the comparative stability of Ascorbic Acid in the lemon is entirely due to the low *p*H of the juice and not to any protective mechanism. In view of the comparative stability of cocoanut water with *p*H between 5 and 6, and the comparative instability of *Citrus decumana* juice with *p*H below 4, Mawson's contention seems untenable. The recent work of Damodaran and Srinivasan [2] with respect to Indian Gooseberry appears to support my results obtained with the cocoanut.

Summary

The Ascorbic Acid concentrations in the juices of Date Palm, Palmyra Palm and Cocoanut Palm have been determined chemically by the 2 : 6 dichlorophenol-indophenol reagent. These juices have been found to be stable even under fermentation.

The Anti-scorbutic property of the cocoanut fruit has been established by physiological experiments on guinea pigs.

The Ascorbic Acid contents of different *Gurs*, obtained by boiling Date Palm juice, have been found to be very high.

Indications have been found of the presence of a mannose dehydrogenase in the juices of the different Palms.

The presence of a certain thermo-labile protective agent for the Ascorbic Acid in cocoanut water has been established.

Investigations on the transference of Ascorbic Acid from water to the kernel and from the kernel into the growing

[1] Mawson, *Biochem. J.*, vol. xxix (1935), p. 569.
[2] Damodaran and Srinivasan, *Current Science*, vol. iii, p. 553.

embryo via the follicle have been carried out. That Ascorbic Acid plays a very important part in the growth of the embryo has also been established by observing the growth of isolated embryo in an Ascorbic Acid medium.

It has been found that green cocoanut fibre exerts a destructive action on Ascorbic Acid.

Investigations have also been carried out in regard to the stability of Ascorbic Acid in the cocoanut water and kernel in contrast with the instability of the Ascorbic Acid present in the juice of *Citrus decumana*.

I take this opportunity of expressing my grateful thanks to Sir J. C. Bose and Prof. N. C. Nag for their interest and helpful criticism during the course of this investigation.

X.—HUMAN REMAINS FROM A MĀLÉR CEMETERY

BY

SASANKA SEKHER SARKAR, M.Sc.

IN September 1935 last, while carrying out an Anthropometric Survey of the Mālér tribe, I came across a small cemetery at Dānowār, a village in Rājmahal Subdivision about 14 miles west of the Tinpahar railway station on the East Indian Railway loop line. Though the bone remains are few in number, in view of the anatomical peculiarities in some of the specimens and the fact that skeletal remains of the Mālér tribe have not been described before, it seemed that it would be worth while to publish a short account of the specimens. The bones

FIG. 58. Typical Mālér Burial.

described below were lying exposed in the cemetery [1] (fig. 58 shows a typical grave from this particular cemetery), but the rest of the skeleton was missing.

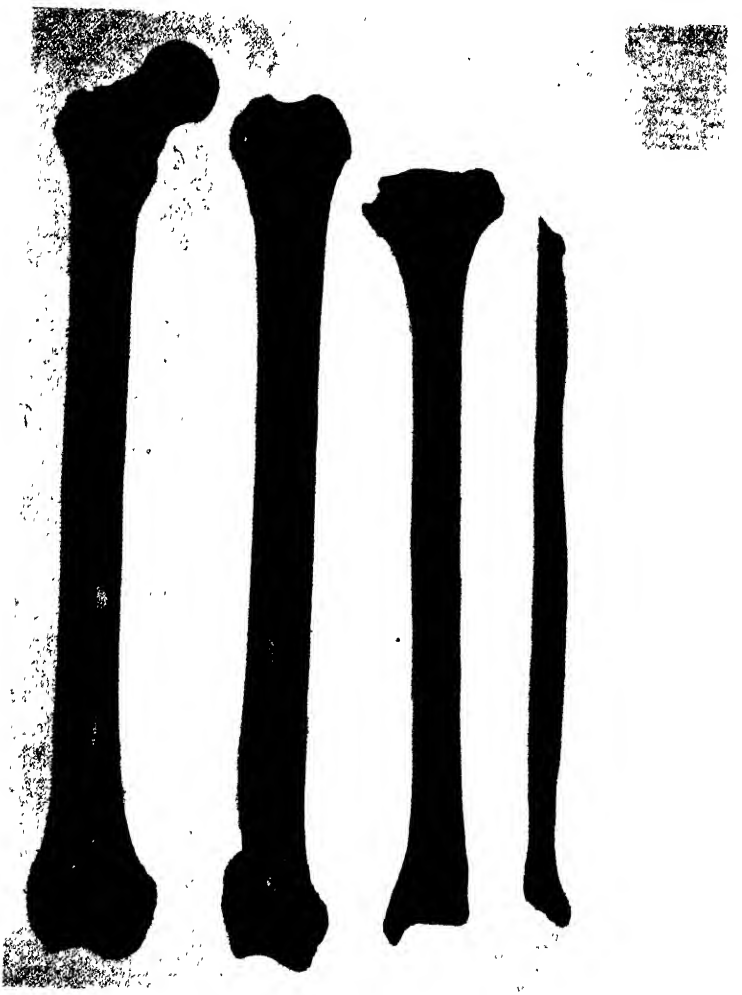

FIG. 59. Anterior view of the skeletal remains.

[1] The Mālérs keep a separate piece of land for burial outside the village. The dead body in Rājmahal Subdivision is buried with the head towards the north; persons dying of smallpox are, however, not buried, but are simply exposed in the cemetery.

The Remains

The skeletal remains (figs. 59 and 60) discovered consist of two femora, the left tibia, and the upper third of

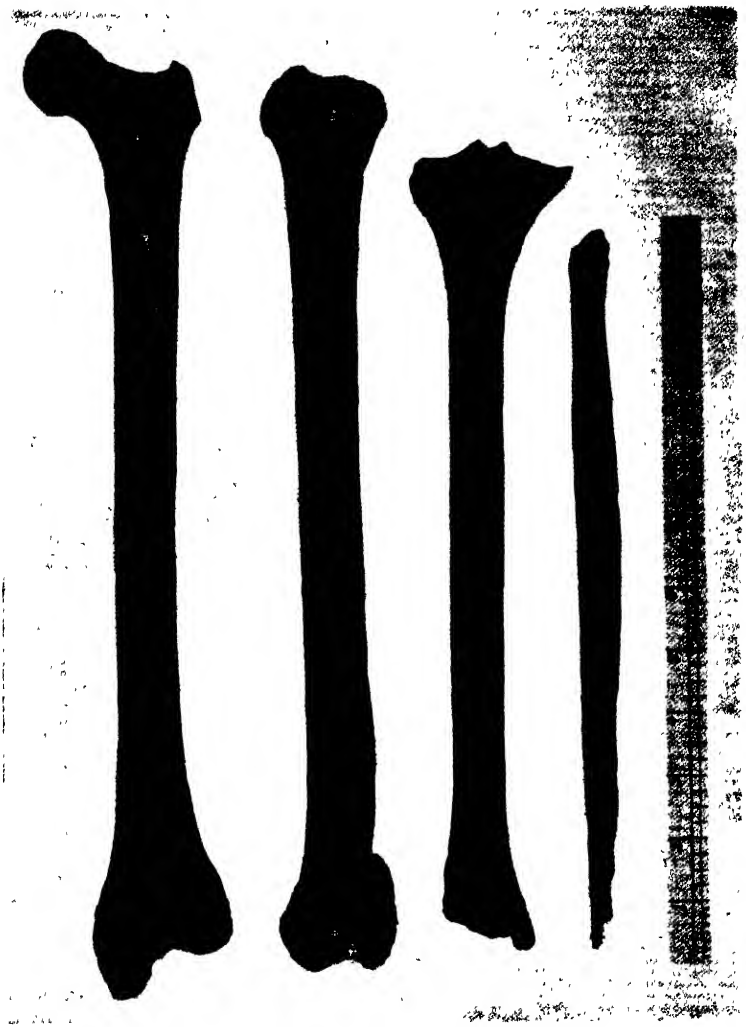

Fig 60 Posterior view of the skeletal remains.

the left fibula. Due to exposure the bones are somewhat worn out at the extremities, but otherwise they are in a good state of preservation.

(*a*) Femora

Of the femora, the right one is complete, while the left has lost its articular head and neck; the two trochanters in both femora are missing and the medial condyle with about 5 cm. of the upper shaft in the case of the left is missing. Only a very limited number of measurements could, therefore, be taken on the left femur. Both femora possess the

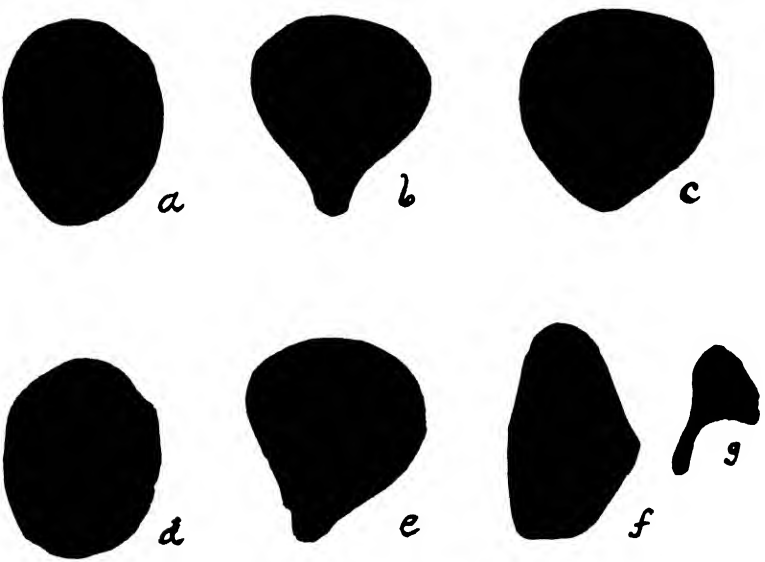

Fig. 61. Cross-sections through the long bones. Right Femur: *a*—proximal; *b*—medial; *c*—distal. Left Femur: *d*—proximal; *e*—distal; *f*—cross-section through the Tibia; *g*—cross-section through the Fibula.

hypotrochanteric fossa, situated on the posterior side of the bone, and this is more marked on the left than on the right. It can be clearly seen in the optical section[1] (fig. 61, *a*, *d*). The hypotrochanteric fossa is separated by a crista hypotrochanterica[2] 5 mm. above the former.

The bones are, on the whole, slender, and the muscular

[1] The optical section has been taken according to the method described by Sewell and Guha, *Memoirs of the Archæological Survey of India*, 'Excavations in Baluchistan,' Appendix V, 'Report on the Bones excavated at Nal,' p. 71.

[2] Martin, R., *Lehrbuch der Anthropologie*, Band II, p. 1149.

impressions are not prominent. The Platymeric Index is 82·14 in both femora. The pilaster is moderately developed and the values of the index are 96·30 and 89·66 in the right and left respectively. The following are the measurements taken on the above bones:

No.	Measurements (in mm.)	Right	Left
	A. Length		
1.	Absolute length	399	—
2.	Physiological length	387	—
3.	Trochanteric length	375	—
4.	Diaphysial length	362	359
	B. Shaft		
5.	Proximal dorso-ventral diameter	23	23
6.	,, medio-lateral diameter	28	28
7.	Medial dorso-ventral diameter	27	29
8.	,, medio-lateral diameter	26	26
9.	Circumference of the shaft (medial)	81	83
	C. Proximal End		
10.	Oblique proximal length	75	—
11.	Length of head and neck	54	—
12.	Vertical diameter of the head	37	—
13.	Transverse diameter of the head	34	—
14.	Circumference of the head	112	—
15.	Vertical diameter of the neck	25	—
16.	Transverse diameter of the neck	29	—
17.	Circumference of the neck	86	—
	D. Distal End		
18.	Dorso-ventral diameter of the shaft just above the condyles	26	26
19.	Medio-lateral diameter of the shaft just above the condyles	31	29
20.	Greatest medio-lateral breadth across the epicondyles	48	—
21.	Greatest dorso-ventral length of the lateral condyle	47	42·5
22.	Greatest dorso-ventral length of the medial condyle	53	—
23.[1]	Amount of bowing	13	—
24.[1]	Bi-condylar width	56	—

[1] Measurements 23 and 24 have been taken after Parsons, *Journal of Anat. and Phys.*, vol. xlviii, p. 238.

No.	Measurements (in mm).	Right	Left
	E. *Angles*		
25.	Collo-diaphysial angle	125°	—
26.	Condylo-diaphysial angle	75°	—
27.	Angle of torsion	35°	—
	INDICES		
	A. *Caliber*		
1.	Length-circumference index	20·96	—
2.	Length-diameter index	11·11	—
	B. *Shape*		
3.	Platymeric index	82·14	82·14
4.	Pilastric index	96·30	89·66
5.	Popliteal index	83·87	89·66
6.	Index of bowing	3·36	—
	C. *Indices of the Proximal End*		
7.	Head index	91·89	—
8.	Robusticity index	18·35	—
9.	Neck length index	13·95	—
	D. *Indices of the Distal End*		
10.	Epicondylar breadth index	12·40	—
11.	Inter-condylar index	112·77	—
12.	Condylar length index	12.14	—

(*b*) TIBIA

The tibia is in a better state of preservation than the femora. The condyles on both the lateral and medial edges have worn out and the lower malleolus also shows signs of attrition. The crista inter-ossea is very prominent and is continuous all through. The Platycnemic Index is 59·38. The following are the measurements taken on the tibia :

No.	Measurements (in mm.)	Right
1.	Maximum length (spino-malleolar)	339
2.	Maximum length (condylo-malleolar)	336
3.	Physiological length	321

B. *Shaft*

No.	Measurements (in mm.)	Right
4.	Dorso-ventral diameter (proximal)	39
5.	Medio-lateral ,, ,,	23
6.	Dorso-ventral (medial)	32
7.	Medio-lateral ,,	19
8.	Dorso-ventral (distal)	28·
9.	Medio-lateral	19
10.	Circumference of the shaft (middle)	76
11.	Least circumference of the shaft	70
12.	Proximal epiphyseal breadth	65
13.	Sagittal diameter of the distal epiphysis	31

C. *Angles*

14.	Retroversion angle	20°
15.	Inclination angle	14·5°
16.	Bi-axial angle	5·5°

Indices

1.	Platycnemic index	59·38
2.	Caliber index	20·65
3.	Femoro-tibial index	82·95

(*c*) Fibula

The shaft of the fibula is triangular in shape. The distal end being missing, it has not been possible to utilise it for any purpose of measurement. The fibula, however, presents a remarkable development of the inter-osseous crest, along with the deep groove of the tibialis posterior muscle on the postero-medial surface. This can be well ascertained from the section in fig. 61, *g*.

Conclusions

1. It seems probable from the examination of the bones that the individual was a female, of about the age of twenty-five. The proximal epiphysis of the fibula usually joins the shaft at about the age of twenty-five, and in the present case the same method has been applied to ascertain the age. In ascertaining the sex from an examination of the long bones I have taken into consideration, firstly, the vertical diameter of the articular head of the femur. This diameter, according to Dwight[1] (American bodies) and Parsons[2] (Rothwell bones), is below 44 mm. in the case of females and above 48 mm. in

[1] T. Dwight, 'The Size of the Articular Surface of Long Bones, as characteristic of Sex,' *American Journal of Anatomy*, vol. iv, p. 19.

[2] F. G. Parsons, 'The Characters of the English Thigh Bones,' *Journ. Anat. and Phys.*, vol. xlviii, p. 238, and vol. xlix, p. 354.

the case of males. Holtby,[1] working in Dublin, showed that the male femora have usually a vertical diameter above 46 mm. Pearson and Bell[2] have re-examined the data of Dwight and Parsons, and working on the London seventeenth-century femora they have deduced that the males have a vertical diameter above 45·5 mm. and the females below 41·5 mm. In the present case the vertical diameter of the articular head is 37 mm., which is much below the figures recorded by the above workers for the females.

That the skeleton was that of a female seems probable also from the following measurements:

(ii) The bicondylar width of the femur of the Mālér specimen is 56 mm., which, according to Parsons and Pearson-Bell, are below 70 mm. and 72 mm. respectively.

(iii) The maximum length of the Mālér femur is 399 mm., Parsons' limit being 400 mm.

(iv) The trochanteric length of the Mālér femur is 375 mm., which, according to Pearson,[3] is below 390 mm. in females.

2. The statures, calculated from the right femur and the left tibia according to Manouvrier[4] and Karl Pearson's[5] formulæ for females, are as follows:

Bone	Pearson		Manouvrier	
	Length	Stature	Length	Stature
		mm.		mm.
Femur . .	399 (Abs.)	1505	389 (Phy.)	1492
Tibia . .	336 (Cond. Mal.)	1548	341 (Sp.-mal.)	1573
Femur + Tibia	735	1519	—	—

[1] J. R. D. Holtby, 'Some Indices and Measurements of Modern Femur,' *Jour. Anat. & Phys.*, vol. lii, p. 379.

[2] Karl Pearson and Julia Bell, 'A Study of the Long Bones of the English Skeleton,' Pt. I, Sec. I & II (Cambridge, 1919), p. 51.

[3] Pearson has mentioned the inapplicability of his results on any other data (*loc. cit.*, p. 56), but as the present collection is very small all available results have been compared.

[4] L. Manouvrier, *Mém. de la Soc., d'Anth. de Paris*, Tome IV, p. 347.

[5] K. Pearson, 'On the Reconstruction of the Stature of Pre-historic Races,' *Phil. Trans.*, vol. 192 (1899), A, p. 186.

The average stature, therefore, comes to 1524 mm. according to Pearson and 1512·5 mm. according to Manouvrier.[1] Neither of these averages agrees with the average stature of the present living Mālér women, which, based on the average of eight individuals, comes to 1459·5 mm.; these samples, however, are too few to draw any definite conclusions.

3. Manouvrier is of the opinion that platymeria, the presence of the hypo-trochanteric fossa in femur, and the presence of platycnemia in tibia is due to life in mountainous regions. The Mālérs also live on hills, and the present village is about 500 ft. above sea-level.

4. The marked development of the inter-osseous crest of the fibula appears also to be due to the above hill-climbing habits. The calf muscles of these people, and particularly the females, are very well developed; for carrying heavy loads of fuel from the jungle to the neighbouring market often falls on the womenfolk among these people.

In conclusion, my grateful thanks are due to Sir J. C. Bose, Kt., F.R.S., for his kind support and encouragement. I also tender my best thanks to Dr. B. S. Guha, M.A., Ph.D., Anthropologist, Zoological Survey of India, for his kind permission to take measurements of the above skeletal remains in his laboratory as well as for his valuable suggestions in preparing this paper.

[1] According to Manouvrier living height is 20 mm. less than the cadaveral height, so 20 mm. has been deducted from the average, which is 1532·5 mm.

XI.—THE SPECTRUM OF ZINC AT DIFFERENT STAGES OF IONISATION

BY

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INTRODUCTORY

THE present investigation was suggested by the appearance of a large number of lines as 'tip lines' in the condensed spark spectra of copper and zinc in the quartz region. The lines are confined to the neighbourhood of the electrodes when the spark gap is of appropriate length. These are quite unlike the lines belonging to the neutral and singly-ionised atoms photographed on the same plate, as the latter have uniform intensity throughout their full lengths. This suggests that the origins of the tip lines lie in more highly ionised atoms, Cu^{++}, Zn^{++}, or Zn^{+++}, etc.

The groups of lines originating from the more important electronic configurations of Cu^{++} and Zn^{+++} were, however, expected in the region of shorter wavelengths. The spectra in the Schumann region were, therefore, investigated by means of the vacuum spectrograph at the Imperial College, London. The excitation of the spectra was caused by sparks in hydrogen. The region investigated at the above college extended from λ 2800 to 1300A. The complex natures of the spectra, however, made it necessary to extend the investigation further down in the ultra-violet. This was carried out in the Physical Laboratory of the Upsala University, Sweden, by means of the 'grazing incidence' spectrographs.

The spectra were excited by condensed 'hot spark' and the region investigated extended from λ 2200 to below 400A. About 750 CuIII lines and a large number of ZnIV lines were photographed and measured. The observational material obtained is exhaustive for the region

examined, the determinations of wavelengths and intensities of the lines are of a very high degree of accuracy, as the most up-to-date technique for work of this nature has been made use of. It is hoped that this part of the investigation is a great step forward in undertaking the elucidation of the structures of the two very complicated spectra CuIII and ZnIV, and the data collected will be ample for locating the terms arising out of the important electronic configurations of the respective atoms.

The spectrum of zinc, however, contained a large number of new lines other than those attributed to the Zn^{+++} atoms. By the method of insertion of inductance in the spark circuit, the different kinds of lines were distinguished from one another. These lines can be attributed with certainty to either ZnIII or ZnII spectra. It has been deemed necessary, before proceeding with the analysis of the ZnIV spectrum, to account for the new ZnIII and ZnII lines obtained. The structure of the ZnII spectrum is fairly well known, but only a small part of the ZnIII spectrum has been classified. With the help of the material obtained it has been possible to extend very considerably the knowledge of the structures of these spectra. The work has been divided into two parts; in the first part ZnII spectrum is discussed and in the second, ZnIII.

Experimental

The earlier photographs of the zinc spectrum were taken with quartz spectrographs and vacuum grating spectrograph at the Imperial College, the source being a strong condensed spark in air or hydrogen. In the quartz region the spectrum is remarkable for the appearance of a large number of lines in the region λ 2600 to 2370A which are confined to the neighbourhood of the electrodes when a suitable spark gap is used (Plate I, fig. 62). The behaviour of these lines suggests that they represent a higher stage of ionisation than that indicated by the lines of ZnII. Some of these lines appear in the tables of spark lines given by Eder and Valenta and by Exner and Hascheck (Kayser's ' Handbuch,' vol. 6, pp. 858–60).

In the Schumann region the spectrum of the zinc spark, like that of the copper spark, is also very complicated, and after many trials it seemed unlikely that the classification

of these lines could be reached until the spectrum in the extreme ultra-violet had been more completely analysed than in the work of Laorte and Lang. Through the kindness of Prof. Siegbahn photographs of the spectra of zinc, copper, silver and cadmium in the extreme ultra-violet were taken in the Physical Laboratory at Upsala with two 'grazing incidence' spectrographs. In one, the grating is of radius 1·5 metres and in the other, 1 metre. The source employed there was the 'hot spark' produced by evacuating the spark chamber and charging the electrodes by means of rectified and condensed current of tension about 50 to 70 kilo-volts. When the evacuation is sufficiently high, only 15 to 20 sparks per minute pass between the electrodes; with each spark the condenser is partially discharged and it takes some time before it can build up the tension again. In the meantime the pump attached to the chamber removes the traces of gases produced with each spark.

The range of spectrum covered by these photographs is from λ 2200 to 400A, the dispersion varying from 5·71A per mm. at 2200A to 2·83A per mm. at 400A. The definition is extremely good and the lines as close as 0·10A are clearly separated. Incidentally, it may be mentioned that the Schumann plates used for photographing all these different spectra at Upsala were prepared by the writer himself. These plates compare very favourably with the

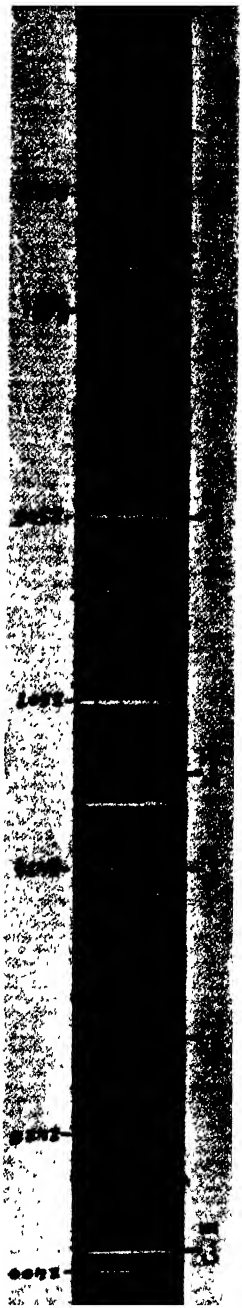


Plate I. Fig. 62. Cu-Spark (Quartz Spect.)

Plate II. Fig. 63. Zinc Spark. * No Inductance. † Inductance.

commercial products, and have the advantage of being fresh.

The lines belonging to the different stages of ionisation were distinguished from each other by introducing a suitable amount of inductance in the spark circuit. First suggested by Prof. A. Fowler in 1925, it has since been extensively used for classifying lines. The insertion of inductance in a spark circuit imparts an arc character to the spark inasmuch as it enhances the lines of lower stage of ionisation, suppressing those of higher stage. Only traces of ZnII lines could be found on the plate when there was no inductance in the circuit, but they became quite prominent when inductance was introduced. By adjusting the time of exposure and the inductance the lines of ZnIII could be obtained with approximately the same intensity with and without inductance. ZnIV lines were prominent without inductance and suppressed with inductance. The reverse was the case with the ZnII lines. The fundamental groups of lines of ZnII, namely the $4s - 4p$ and $4p - 4d$ groups, though quite bright in both cases, were much more so when there was induction. The typical example regarding the behaviour of the ZnII lines is the $4s - 5p$ group, 101612 cm.$^{-1}$ and 101367 cm.$^{-1}$, the intensities of these lines being '3' and '0' with and without inductance respectively—the intensity of the prominent lines of ZnIII classified by Laporte and

Lang being taken as '10.' A typical photograph is reproduced in Plate II, fig. 63.

The standard lines used in these investigations were the lines belonging to O, N and C with different degrees of ionisation. Many of these lines appeared as impurity lines on the plate and were investigated very exhaustively by Edlēn and others. The lines due to O and N, when necessary, were produced and photographed on the same plate, and partly overlapping the Zn spectrum, by means of sparks between the upper Zn-rod and a lower Al-rod at the tip of which a little lithium nitrate had been fused. The lower poles could be placed in position by simply rotating the cone containing them without letting any air enter into the spark chamber or the spectrometer. All the Al lines from 1990·534 to 1352·587A determined by Bowen and Ingram (*Phys. Rev.*, vol. 28, 1926) were also produced in this way and could be used as standard lines. Some of these Al lines were always present on the plate even when no Al-rod was used.

The grating having been mounted at nearly tangential incidence, the dispersion varies considerably from point to point. It has been, therefore, necessary to use the ordinary grating formula,

$$m\lambda = e \sin \varphi - e \sin \left(\varphi - \frac{x}{R}\right)$$

for computing the wavelengths (e is the grating space, φ, the angle of incidence, and x, the distance from the directly reflected image). This method has been developed at Upsala and a brief description is given below.

Three standard lines are chosen, one from each end and the third from the middle part of the region concerned. Let these lines be λ_1, λ_2 and λ_3 and the corresponding micrometer settings x_1, x_2 and x_3. The dispersion for the points, $x_1 + \frac{x_2 - x_1}{2}$ and $x_2 + \frac{x_3 - x_2}{2}$ are

$$\left(\frac{\Delta\lambda}{\Delta x}\right)_1 = \frac{\lambda_2 - \lambda_1}{x_2 - x_1}$$

and

$$\left(\frac{\Delta\lambda}{\Delta x}\right)_2 = \frac{\lambda_3 - \lambda_2}{x_3 - x_2}$$

respectively.

The change in the dispersion for the interval,

$$(\Delta x^2) \equiv \left(x_2 + \frac{x_3 - x_2}{2}\right) - \left(x_1 + \frac{x_2 - x_1}{2}\right)$$

is

$$\left(\frac{\Delta\lambda}{\Delta x}\right)_2 - \left(\frac{\Delta\lambda}{\Delta x}\right)_1 \equiv \Delta^2\lambda$$

Therefore the rate of change of dispersion for the point,

$$(\equiv x),\ x_1 + \frac{x_2 - x_1}{2} + \frac{\Delta x^2}{2},$$

is equal to $\frac{\Delta^2\lambda}{\Delta x^2}$. This quantity can be shown to be equal to $C - \frac{\lambda}{R^2}$ by differentiating twice the grating equation given above; C is a constant, λ the wavelength for the point, x, and R the radius of the grating. λ can be obtained from the graph drawn by plotting the standard lines against the respective micrometer settings, thus the constant, C, is determined. C and R being now known, $d^2\lambda/dx^2$ can be calculated for different values of λ and a table constructed. A table for dispersion is then made, starting from the point, say, $x_1 + \frac{x_2 - x_1}{2}$, for which it is already known, adding or subtracting $d^2\lambda/dx^2$ as the case may be, for the successive intervals of 1 mm. The wavelengths are now calculated starting from λ corresponding to integral value of x next to x_1, λ_1 and the dispersion in the neighbourhood of x_1 being known. The λ's corresponding to integral values of x are then determined by adding up successively the dispersions given in the table mentioned. These wavelengths are hypothetical. For actually calculating the wavelengths a standard line is chosen and the value of x corresponding to it is then calculated from the table; the micrometer readings for all other lines are accordingly changed. The wavelength for the line next to this standard line is obtained by adding to it the product of the interval between them and the dispersion in the neighbourhood, and so on. The usual correction is then applied. The same table can be used for different plates provided that the setting of the instrument has not been changed.

PART I.—THE SPECTRUM OF SINGLY-IONISED ZINC (ZnII)

CLASSIFICATION

Singly-ionised zinc is isoelectronic with neutral copper and its spectrum consists of a doublet system of terms arising from the normal configuration $3d^{10}4s$, etc., and quartet and doublet systems from the anomalous configurations $3d^{9}4s^{2}$, etc. The important electronic configurations and the corresponding terms are given in Table I.

TABLE I

4_1 4_2 4_3 4_4

Prefix	Terms
$3d^{10}4s$	$^2S_1$
$3d^{10}4p$	$^2P_{2,1}$
$3d^{10}4d$	$^2D_{3,2}$
$3d^{10}4f$	$^2F_{4,3}$
$3d^{10}ns$	$^2S_1$
$3d^{10}np$	$^2P_{2,1}$
$3d^{10}nd$	$^2D_{3,2}$
$3d^{10}nf$	$^2F_{4,3}$
$3d^{9}4s^{2}$	$^2D_{3,2}$
$3d^{9}4s4p$	^{4}(PDF) ^{2}(PDF)
$3d^{9}4sns$	^{4}D ^{2}D

The spectrum was first investigated by Von Salis (*Ann. Phys.*, vol. 76 (1925), p. 150). A large number of terms arising from the configurations $3d^{10}n$ (s, p, d, f) and $3d^{9}4s^{2}$ were identified in that work. This investigation extended from λ 7757·97 to 2026·19A and some of the lines given by combinations of the above terms were not located. A few of these lines, however, were found by Lang (*Proc. Nat. Aca. Sc.*, vol. 15 (1929), p. 413). Takahasi studied the problem again by exciting the spectrum by the hollow cathode method (*Ann. Phys.*, vol. 3 (1929), p. 27). The region investigated by Takahasi extended from λ 5165 to 833 A. Besides obtaining the lines either found in or predicted by the work of Von Salis, Takahasi obtained a large number of additional lines. Some of these new lines were provisionally classified as due to the combination of terms A(n) and B(n) with one another or with the terms found by Von Salis.

In connection with his work on ZnIV and ZnIII the present writer has observed a number of lines belonging to ZnII which had not been recorded previously. An account

of these lines and of their classifications is given in what follows.

The doublet system of terms shown in Table I, including $3d^9 4s^2$ ($^2D_{3,2}$) have been identified by Von Salis. In the case of CuI, which is isoelectronic with ZnII, besides these terms, the terms arising out of the configurations $3d^9 4s 4p$ and $3d^9 4s 5s$ have been found by Shenstone (*Phys. Rev.*, vol. 28 (1926), p. 449), the latter giving rise to negative terms only. Shenstone found an additional 11 positive terms and a large number of negative ones, but these terms have not yet been designated. They may perhaps belong to the configurations $3d^9 4p 5s$, $3d^9 4p^2$, $3d^8 4s^2 np$, etc.

TABLE II

		$3d^{10}4s$ $^2S_1$ 144890	$3d^9 4s^2$ $^2D_3$ 82169	$3d^9 4s^2$ $^2D_5$ 79450	$3d^{10}5s$ $^2S_1$ 56454	a_2 3929	CuI $\Delta\nu$
$3d^9 4s 4p$							
41188	$^4P_3$		40981	*			
39570[1168]	$^4P_2$	105321 (N?)	42598	39879			1095
38364[1206]	$^4P_1$	106525		41087			830
	$^4F_5$						
34663	$^4F_4$		47506				
34276[387]	$^4F_3$		47893	*			410
A(3) 32899[1377]	$^4F_2$	111993	49268	46552			740
33622	$^4D_4$		48547				
32482[1140]	$^4D_3$		49687	*			892
A(4) 32368[114]	$^4D_2$	112524	*	47080			138
A(5) 32311[57]	$^4D_1$	112591		47138			377
A(6) 31394	$^2P_2$	113497	50778	48050		25060	
30282[1112]	$^2P_1$	114608		49167			64
A(7) 30848	$^2D_3$		51321	48602			
A(8) 30059[789]	$^2D_2$	114830	52113	49395 (III ?)			425
31359	$^2F_4$		50810				
28998[2361]	$^2F_3$		*	50452			1237
21374	d_2		60798	58074			
16754	e_3		65418	62693			
16549	f_2	128339	65622				
14522	g_2	130368	67647			41934	
12480	h_1	132408		66973			
11082	k_1	133810		68365			
10249	l_2	134644	71920	69202 (III ?)			
186	m_1			79265		56267	
−1162	n_0	146063				57616	

* Missing intercombination.

Some new lines of ZnII in the region of short wavelength having been found by the present writer, it has been possible to identify the terms $3d^9 4s 4p$(4, 2(PDF)). They

include some of the undesignated A(n) terms given by Takahasi. Ten more terms (undesignated) have also been found. No attempt has been made to locate the terms $3d^9 4s5s$; these will give lines in the region of longer wavelengths by combining with the $3d^9 4s4p$ group, and only a few lines have been recorded in the expected region.

In Table II are given the new terms and the lines obtained by their possible combinations with $3d^{10}4s\ ^2s_1$ and $3d^9\ 4s^2\ ^2(D_{3,2})$ found by von Salis. The term values shown in the table are based upon $3d^{10}4s\ ^2s_1 = 144890$ given by von Salis. The terms marked ' A(n) ' are the undesignated terms of Takahasi. No confirmatory combinations have been found for some of these terms and they can only be suggested by comparing with the corresponding terms of CuI. The differences characteristic of the latter are given on the right of the table for comparison.

It may be noted here that the classification of some of the ZnII lines suggested by Lang appear to be doubtful. Thus the two lines classified as $3d^{10}4s\ ^2s_1 - 3d^9 4s^2\ ^2D_3$ and $3d^{10}4s\ ^2s_1 - 3d^9 4s^2\ ^2D_2$ would violate the l-combination rule and the former would also violate the j-combination rule. The predicted wave number for the line $^2s_1 - ^2D_3$ is 62721, but the writer could not find a line in this position. The line 62693 cm.$^{-1}$ adopted for this combination by Lang appeared on the writer's plate with intensities ' 2 ' and ' 1 + ' with and without inductance, so judging by the wave number and intensity the line cannot be identified with the $^2s_1 - ^2D_3$ combination. The combination $^2s_1 - ^2D_2$ would give the wave number 65440 cm.$^{-1}$. The writer found a line with the wave number 65446 cm.$^{-1}$, but as the intensities were ' 3 ' and ' 2 ' with and without inductance, it is not likely to be a ZnII line. The line 65418 cm.$^{-1}$ suggested by Lang to be $^2s_1 - ^2D_2$ was of intensities ' 1 ' and ' 0 + ' with and without induction and is, therefore, more likely to be a ZnIII line than ZnII one. All these three lines 62693, 65418 and 65446 were, however, brighter with inductance in circuit, which was not generally the case with the ZnIII lines. This suggests that the lines are probably blends of ZnII and ZnIII lines. The line 65446 cm.$^{-1}$ being nearer the predicted wave number 65440 cm.$^{-1}$, is provisionally classified as due to the combination $^2s_1 - ^2D_2$. The other two lines whose wave number difference, 2725, is approximately equal to that of the $3d^9 4s^2\ ^2(D_{3,2})$ terms

but which are out of the predicted positions, as has been pointed out by Lang, by 28 and 22 units, are here classified as due to the combinations of a new term, c_3, with the $3d^9 4s^2$ terms.

There are several more discrepancies between the observations of Lang, Takahasi and the writer, as will appear from Table III. In this table are listed the 11 lines located by Lang which were predicted by the work of von Salis, and all the lines observed by Takahasi in the region 44840 to 146063 cm.$^{-1}$. Takahasi's paper contains many more lines on the longer wavelength side of the above region which are not included in this list. Some of these lines have, however, been used by the writer for the classification given in Table II. In the column headed ' Maz.' in Table III are given the lines observed by the writer in the above region. The lines which are distinctly of ZnIII and ZnIV origin have been excluded, excepting those the observations regarding which are in conflict. In the column ' ionisation ' are given the stages of ionisation of the respective lines found experimentally in the present investigation. On the right of the table is given the classification whenever identified. The letter ' M ' has been placed against the new classification assigned by the present author.

The lines 63232, 66405 and 67871 cm.$^{-1}$ have been classified by Laporte and Lang (*Phys. Rev.*, vol. 30 (1927), p. 378), as due to the combinations $4s^3D_3 - 4p^3F_4$, $4s^3D_3 - 4p^3D_3$ and $4s^3D_3 - 4p^1F_3$ respectively of the ZnIII spectrum, and this is confirmed by the author's experiment. Takahasi, however, has included them in his list of ZnII lines. It seems improbable that these bright lines belonging to the fundamental group of ZnIII lines, the line 63232 cm.$^{-1}$ being the brightest in the whole spectrum, have been completely suppressed in the spectrum excited by the hollow cathode method and in their places ZnII lines have made their appearance.

TABLE III

Lang	Int.	Takahasi	Int.	Maz.	Int. With Ind.	Int. Without Ind.	Ionisation	Classification	
		44840	000	44846?	0+	0	II		
		45231	3	45233	0+	0+	III		
		46359	00						
		46552	3	46554	0+	0	II	$3d^9\,(4s^2\,{}^2D_2-4s4p\,{}^4F_2)$	M
		47080	00					$3d^9\,(4s^2\,{}^2D_2-4s4p\,{}^4D_2)$	M
		47091	0	47092	1	1	III		
		47138	00					$3d^9(4s^2\,{}^2D_2-4s4p\,{}^4D_1)$	M
		47212	00						
		47472	000						
				47506	1	0+	II or III	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^4F_4)$	M
		47672		47671	0	0	III or IV		
				47675	2	1	III		
				47893	1	0	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^4F_4)$	M
		47949	1·5	47940	0	0+	III or IV		
		48004	00						
		48026	000						
		48050	000					$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2P_2)$	M
		48081	00	48082	1	0+	II or III		
		48143	1						
				48547	0+	0	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^4D_4)$	M
		48602	15	48602	1+	0+	II or III	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2D_3)$	M
		49020	10	49012	1	1	III		
				49103	1−	0+	II or III		
				49167	1−	0	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2P_1)$	M
		49268	00					$3d^9(4s^2\,{}^2D_2-4s4p\,{}^4F_2)$	M
		49391	2	49395	0	0	IIIorIV*	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2D_2)$	M
		49686	10	49687	2	0	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^4D_2)$	M
		49768	00	49770	0	2	IV		
				50452	2	0+	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2F_2)$	M
		50775	2	50778	1+	0	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2P_2)$	M
				50810	0+	0	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2F_4)$	M
		51321	1					$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2D_2)$	M
51816	1	51822	1	51819	0+	0+	III*		
		52110	10	52113	3	1	II	$3d^9(4s^2\,{}^2D_2-4s4p\,{}^2D_2)$	M
		54446	8						
		54517	3	faint			II	$3d^9 4s^2\,{}^2D_2-3d^{10}6p\,{}^2P_2$	
54534	2	54542	1·5	54539	4	0+	II	$3d^9 4s^2\,{}^2D_2-3d^{10}4f\,{}^2F_4$	
				55217	2	0+	II		
				56267	1+	0	II	$3d^{10}5s\,{}^2S_1-m_1$	M
		57236	20	57236	0+	0	IIorIII*	classified as III	M
								$3d^9 4s^2\,{}^2D_2-3d^{10}6p\,{}^2P_2$	
				57616	2	0	II	$3d^{10}5s\,{}^2S_1-n_0$	M
				58074	0+	0	II or III	$3d^9 4s^2\,{}^2D_2-d_2$	M
				58577	2	1	II or III		
		59770	000						
				60349	2	0	II		

* Probably includes lines of ZnII.

TABLE III (*continued*)

Lang	Int.	Takahasi	Int.	Maz.	Int. With Ind.	Int. Without Ind.	Ionisation	Classification	
		60798	000					$3d^9 4s^2\ ^2D_3 - d_3$	M
		61379	0						
62693	2			62693	2	1+	II or III	$3d^{10} 4s^2\ ^2S_1 - 3d^9 4s^2\ ^2D_3$	L
		63072	00					$3d^9 4s\ ^2D_2 - e_3$	M
		63226	0	63232	12	10	III	classified as III $3d^9 4s^2\ ^2D_2 - 7p\ ^2P_2$	T
64485	1	64474 (C?)	0	64484	0	8	C IV	$3d^9 4s^2\ ^2D_3 - 3d^{10} 5f\ ^2F_4$	L,T
				64656	2	1	II or III		
65142	3	65137	20	65141	3	1	II	$3d^{10} 4p\ ^2P_2 - 3d^{10} 6s\ ^2S_1$	
65416	1			65418	1	0+	II or III	$3d^{10} 4s\ ^2S_1 - 3d^9 4s^2\ ^2D_2$ $3d^9 4s^2\ ^2D_3 - e_3$	L M
				65446	3	2	III or II?	$3d^{10} 4s\ ^2S_1 - 3d^9 4s^2\ ^2D_2$	M
				65494	2	1+	III		
		65618	1	65622	3	1	II	$3d^9 4s^2\ ^2D_3 - f_2$	M
66015	1	66017	10	66016	2	1−	II	$3d^{10} 4p\ ^2P_1 - 3d^{10} 6s\ ^2S_1$	
		66208	00	66208	4	2	II		
				66282	2	1+	III		
		66405	00	66405	8	8	III	Classified as III	
				66973	3	1	II	$3d^9 4s^2\ ^2D_2 - h_1$	M
				67015	2	1	II or III		
		67162	0000					$3d^9 4s^2\ ^2D_2 - 3d^{10} 6f\ ^2F_3$	
		67292	1	67292	6	5	III		
				67468	2	1	II or III		
		67486	000	67483	0	2	IV		
		67646	0	67647	5	3	II or III	$3d^9 4s^2\ ^2D_2 - g_2$	M
		67869	00	67871	10	10	III	Classified as III	
				67940	1	0	II		
				68365	2	0+	I	$3d^9 4s^2\ ^2D_2 - h_1$	M
		68615	10	68614	3	0+	II	$3d^{10} 4p\ ^2P_2 - 3d^{10} 5d\ ^2D_2$	
		68640	50	68638	3	1	II	$3d^{10} 4p\ ^2P_2 - 3d^{10} 5d\ ^2D_3$	
				68673	1	0	II		
		68926	0	68928	4	3	III		
		69201	0	69202	4	3	III*	$3d^9 4s^2\ ^2D_2 - l_2$?	M
		69487	30	69488	5	2	II	$3d^{10} 4p\ ^2P_1 - 3d^{10} 5d\ ^2D_2$	
		69890	000	69887	0+	0	II	$3d^9 4s^2\ ^2D_3 - 3d^{10} 6f\ ^2F_3$	
				70426	4	2	II		
				71920	1	0	II	$3d^9 4s^2\ ^2D_2 - l_2$	M
				73597	1	0	II		
76529	3	76525	1	76530	2	5	IV*	$3d^{10} 4p\ ^2P_2 - 3d^{10} 7s\ ^1S_2$	
				78280?	0	0	II	$3d^{10} 4p\ ^2P_2 - 3d^{10} 6d\ ^2D_2$	M
				78294	2	0	II	$3d^{10} 4p\ ^2P_2 - 3d^{10} 6d\ ^2D_3$	M
		79150	0000	79154	2	0	II	$3d^{10} 4p\ ^2P_1 - 3d^{10} 6d\ ^2D_2$	
				77386	4	3	III		
77408	1	77400	0	77413	1	4	IV	$3d^{10} 4p\ ^2P_1 - 3d^{10} 7s\ ^2S_1$	L,T

* Probably includes lines of ZnII.

TABLE III (*continued*)

Lang	Int.	Takahasi	Int.	Maz.	Int. With Ind.	Int. Without Ind.	Ionisation	Classification	
		79265	00					$3d^9 4s^2\ {}^2D_2 - m_1$	M
		79308	000						
		83810	000	83806	1	2	III		
101367	1	101364	2	101367	3	0+	II	$3d^{10}4s\ {}^2s_1 - 3d^{10}5p\ {}^2p_1$	
101612	1	101610	3	101612	3	0+	II	$3d^{10}4s\ {}^2s_1 - 3d^{10}5p\ {}^2P_2$	
		105321	1	105318	1	0+	II or III (N?)	$3d^{10}4s\ {}^2s_1 - 3d^9 4s4p\ {}^4P_2$	M
				106522	2	0	II	$3d^{10}4s\ {}^2s_1 - 3d^9 4s4p\ {}^4P_1$	M
		111993	2	111996	2	0	II	$3d^{10}4s\ {}^2s_1 - 3d^9 4s4p\ {}^4F_2$	M
		112524	1	112538	4	1	I	$3d^{10}4s\ {}^2s_1 - 3d^9 4s4p\ {}^4D_2$	M
		113497	1	113497	6	2	II	$3d^{10}4s\ {}^2s_1 - 3d^9 4s4p\ {}^4P_2$	M
		119875	00				o II?	$3d^{10}4s\ {}^2s_1 - 3d^{10}6p\ {}^2P_1$	T
		119959	2				o III ?	$3d^{10}4s\ {}^2s_1 - 3d^{10}6p\ {}^2P_2$	T
				114608	0+	0	II	$3d^{10}4s\ {}^2s_1 - 3d^9 4s4p\ {}^2P_1$	M
				114830	0+	0	II	$3d^{10}4s\ {}^2s_1 - 3d^9 4s4p\ {}^2D_2$	M
				117434	1	0+	II or III		
				119468	2	0	II		
				120348	2	1	II or III		
				124053	1	0	II (C?)		
				128339	2	0	II	$3d^{10}4s\ {}^2s_1 - f_2$	M
				130368	3	0	II	$3d^{10}4s\ {}^2s_1 - g_2$	M
				132408	2	0	II	$3d^{10}4s\ {}^2s_1 - h_1$	M
				133810	0+	0	II	$3d^{10}4s\ {}^2s_1 - k_1$	M
				134644	1−	0	II	$3d^{10}4s\ {}^2s_1 - l_2$	M
				146063	2	0+	II	$3d^{10}4s\ {}^2s_1 - n_0$	M

SUMMARY

The observations of some new lines in the region of short wavelength have made it possible to identify the $3d^9 4s4p$ (^{4}, ^{2}PDF) terms in the spectrum of singly ionised zinc (ZnII). Ten additional undesignated terms have also been found. The number of lines for which classifications have been assigned is fifty-three. Certain discrepancies between previous observations and those of the present writer are pointed out.

PART II.—THE SPECTRUM OF DOUBLY IONISED ZINC (ZnIII)

This investigation of the spectrum ZnIII has formed part of a more general investigation which was undertaken

in order to extend our knowledge of the spectra at successive stages of ionisation of the zinc atom.

Since doubly ionised zinc is isoelectronic with singly ionised copper and neutral nickel, a general similarity of the three spectra, ZnIII, CuII and NiI, is to be expected. In accordance with Hund's theory, the triplet and singlet terms arising from the atoms in the unexcited and various excited states may conveniently be represented as in Table I (Part II), which indicates the types of terms arising from the more important configuration shown on the left.

TABLE I

3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	Prefix	Terms
2	6	10							$3d^{10}$	$^1S_0$
2	6	9	1						$3d^9 4s$	^1D, ^3D
2	6	9		1					$3d^9 4p$	^{1}(PDF), ^{3}(PDF)
2	6	9					1		$3d^9 5s$	^1D, ^3D
2	6	9			1				$3d^9 4d$	^{1}(SPDFG), ^{3}(SPDFG)
2	6	9						1	$3d^9 5p$	^{1}(PDF), ^{3}(PDF)
2	6	8	2						$3d^8 4s^2$	^{1}(SDG), ^{3}(PF)
2	6	8	1	1					$3d^8 4s 4p$	^{5}(DFG) ^{3}(DFG), etc.

The lines corresponding with the possible combinations of the first three rows have already been measured and identified by Laporte and Lang (*Phys. Rev.*, vol. 30 (1927), p. 378). In the course of the present investigation all the terms shown in the fourth and the fifth rows and a part of the terms arising out of the configurations $3d^8 4s 4p$, have been identified. The terms $3d^8 4s^2$ and $3d^8 4s 4p$ for NiI (Russel, *Phys. Rev.*, vol. 34 (1929), p. 821), have been found to give very bright lines in combination with the $3d^9 4p$ and $3d^9 4s$ terms respectively. No traces of these lines have, however, been found in the case of CuII, though the spectrum was excited by the very powerful method of 'hollow cathode' (Kruger, *Phys. Rev.*, vol. 34 (1929), p. 1122). Nickel being in the transition period, its normal configuration is $3d^8 4s^2$. When excited it gives, besides the terms $3d^9 n(spd)$, the terms $3d^8 nsnp$, as can be expected from its normal configuration. The partial appearance of these lines in the spectrum, ZnIII, is due to the fact that the hot spark used for exciting the spectrum was very powerful; longer exposures would, perhaps, have brought out the fainter lines not obtained in the present investigation.

Classification

There can be no doubt that the strong group of lines, λ 1839 to 1432A, has been correctly classified by Laporte and Lang as arising from the combination of the $3d^9 4s$ group of terms with the $3d^9 4p$ group. The lines occur in the region which is to be expected from a comparison with corresponding groups in the isoelectronic spectra NiI and CuII, as shown by Laporte and Lang in an application of the irregular doublet law. Thus,

	$4s\ ^3D_4 - 4p\ ^3D_3$	
NiI	29464	
		19448
CuII	48912	
		17493
ZnIII	66405	

where the Δν's are in the usual order of agreement in such comparisons. Moreover, the terms of CuII and ZnIII are arranged in the same order of magnitude and the Δν's in the components of triplets have the same sign, namely ' −.'

The expected regions for the $(4p - 5s)$ and $4p - 4d)$ groups of lines were in the neighbourhood of the $(4s - 4p)$ group. On examining the lines just below the $(4s - 4p)$ group a large number of differences characteristic of the $4p$ terms have been obtained. It has been possible to arrange the lines as due to the possible combinations of $4p$ terms with the $5s$ and $4d$ terms.

The two groups of lines appearing between λ 600 and 500A and giving differences characteristic of the $4s$ terms were first thought to be due to the combinations of the $4s$ group with two groups of np terms in the light of the grouping of the $4p$ terms as far as possible. It has, however, been found that these two groups are too close to permit of their being united in a Rydberg sequence of np terms with the $4p$ terms already known. Moreover, the expected region for $4s - 5p$ group is in the neighbourbood of 630A. There are only a few ZnIII lines in this region and it has not been possible to identify the $5p$ terms by means of them. The other alternative for accounting for the two groups of lines in the region λ 600 to 500A is to arrange them as due to the combination of $4s$ terms with the terms arising from the configuration $3d^8 4s 4p$. The configuration $3d^8 4s 4p$ is obtained by adding one p-electron to the configuration

$3d^8 4s$ giving the terms ^{2}(SDG), ^{2,4}(PF). The terms belonging to $3d^8 4s 4p$ which have been found in the case of NiI to give bright lines are the terms ^{1,3}(DFG) and ^{3,5}(DFG) arising from ^{2,4}(F) of $3d^8 4s$. It has been possible to identify the terms ^{1,3}(DFG) and ^{3,5}(DFG) for ZnIII. Some of these terms are provisional on account of absence of corroborative combinations.

The terms $3d^8 4s^2$ ^{1}(SDG) ^{3}(PF) for NiI have been found to give very bright lines by combining with $3d^9 4p$ ^{1,3}(PDF), but they have not been located for ZnIII. The transition concerned being a double electronic one, the lines are perhaps too faint or may lie further in the region of long wavelength not investigated in the present work.

The $4s$ and $5s$ groups having been established, it has been possible to calculate the absolute term values by means of a simple Rydberg formula. The value for the $4s\,^3D_3$ term is found to be 246300 cm.$^{-1}$. This places the deepest term $3d^{10}\,s_0$ at 324405 cm.$^{-1}$; the corresponding ionisation potential is about 40 volts. It may be noted that the value for the $4s\,^3D_3$ term suggested by Laporte and Lang by extrapolating the corresponding values for the isoelectronic spectra NiI and CuII is 247000 cm.$^{-1}$. Thus the agreement is very close.

Comparison of the Three Isoelectronic Spectra NiI, CuII, and ZnIII

It is of interest to compare the term values of isoelectronic spectra NiI, CuII, and ZnIII as in the following table:

The values of the $3d^9 5s(^{3,1}(D))$ *terms*

	$^3D_3$	$^3D_2$	$^3D_1$	$^1D_2$
NiI .	18973 (184)	18789 (1322)	17467 (151)	17316
CuII .	55626 (321)	55305 (1749)	53556 (282)	53274
ZnIII	109520 (462)	109058 (2322)	106736 (185)	106551

The figures for NiI have been taken from Russel (*Phys. Rev.*, vol. 34 (1929), p. 821) and those for CuII from Kruger (*Phys. Rev.*, vol. 34 (1929), p. 1122).

It will be seen that the separations of the terms have systematically increased with the nuclear charge excepting ($^3D_1 - ^1D_2$) which, although of the same order of magnitude, is less than what is to be expected for ZnIII; but

a close analogy does not apply to the difference between a triplet and a singlet term.

Separation of the Triplet D term

	$3d^9 4s$		$3d^9 5s$	
	(1,2)	(2, 3)	(1,2)	(2,3)
NiI . . .	833	675	1322	184
CuII . . .	1151	918	1749	321
ZnIII . .	1576	1178	2322	462

The above figures show that the difference, $^3D_2 - ^3D_1$, has increased with the quantum number, whereas $^3D_3 - ^3D_2$ has decreased. The total separation has, however, remained practically the same. It is evident from this that the separation of the ground terms, $3d^9\ ^2D_{3,2}$ of ZnIV will approximately be $((1576 + 1178) + (2322 + 462))/2$ or 2769 cm.$^{-1}$.

Application of the Irregular Doublet Law

	$4s\ ^3D_3$	$4p\ ^3D_3$	$4s\ ^3D_3 - 4p\ ^3D_3$		$(4s\ ^3D_3)^{\frac{1}{2}} - (4p\ ^3D_3)^{\frac{1}{2}}$ $\Delta(\nu^{\frac{1}{2}})$
NiI .	61374	31910	29264		69·1
				19451	
CuII .	141709	92794	48915		71·8
				17490	
ZnIII .	246300	179895	66405		72·2

According to the irregular doublet law $\Delta\nu^{\frac{1}{2}}$ is independent of the nuclear charge which is found to be approximately the case from the figures given in the last column. The other interpretation of the irregular doublet law asserts that the wave number for the line $4s\ ^3D_3 - 4p\ ^3D_3$ will be a linear function of Z, *i.e.* the difference between the wave number for the line in the consecutive spectra will be the same. It has already been pointed out (p. 195) that this is true. The figures on the right of column 4 also prove the same thing. For comparison, the wave numbers and their differences for the line $4p\ ^3D_3 - 5s\ ^3D_3$, to which the above law does not apply, are given below.

	$4p\ ^3D_3 - 5s\ ^3D_3$	
NiI . . .	12937	
		24234
CuII . . .	37171	
		33206
ZnIII . . .	70377	

The differences in the wave numbers of the line in the consecutive spectra, although of the same order of magnitude, are not even approximately equal.

In fig. 64 the Moseley Diagrams for the terms $3d^{10}\ {}^1S_0$,

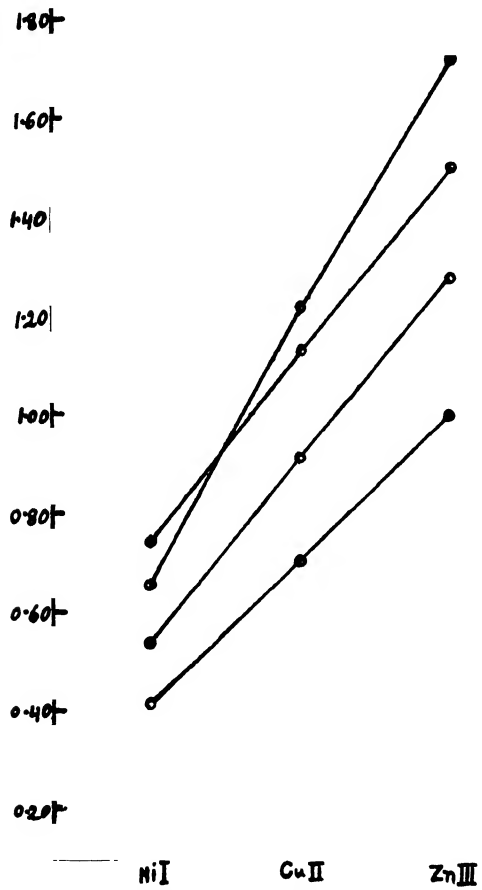


FIG. 64. Moseley diagram for NiI, CuII, ZnIII.

$3d^9\ 4s\ {}^3D_3$, $4p\ {}^3D_3$ and $5s\ {}^3D_3$ for the three isoelectronic spectra NiI, CuII and ZnIII are drawn. The figures for ZnIII are based upon $4s\ {}^3D_3 = 246300$ cm.$^{-1}$ calculated from the data obtained in the present investigation. The

curves corresponding to the term $4s\ ^3D_3$ and $4p\ ^3D_3$ run fairly parallel. All the curves bend slightly downwards with increasing Z; the bending is very small in the case of the $4p\ ^3D_3$ and $5s\ ^3D_3$ terms.

In Table II the wave numbers of the lines classified as due to the combination of $4p$ and $5s$ terms are given. For completeness the $(4s-4p)$ group of lines given by Laporte and Lang is also included. The figures just above the wave numbers indicate the intensities. The term values written near the respective terms are those obtained by the author.

In Table III are given the designation of the terms and the corresponding values; in Table IV, the wavelengths, wave numbers, intensities and classification. The lines against which the letter 'L' has been written are those classified by Laporte and Lang; the wavelengths and wave numbers for these lines are also those given by these authors. These figures are slightly different from those obtained by the present writer, the wave numbers differing by 3 or 4 units. The letter 'M' has been written before some of the 'L's.' The wavelengths and wave numbers corresponding to these are the present writer's. The line 65225 cm.$^{-1}$ $(4s\ ^3D_2 - 4p\ ^3D_3)$ was not, however, found by Laporte and Lang. The corresponding line for CuII was also missed by Shenstone (*Phys. Rev.*, vol. 29 (1927), p. 380); but Kruger succeeded in photographing it by exciting the spectrum by the method of hollow cathode. In the present investigation it has been possible to identify and measure this line (for ZnIII). Its intensity is only '1' but it ought to have been as great as '3' according to Laporte and Lang. These authors could not also separate the lines $4s\ ^3D_3 - 4p\ ^3F_2$ and $4s\ ^3D_1 - 4p\ ^3D_2$, but the present writer has succeeded in doing so. The wave numbers corresponding to the lines $3d^{10}\ ^1S_0 - 3d^9 4p\ ^3D_1$ and $3d^{10}\ ^1S_0 - 4p\ ^1P_1$ were longer by 14 units in the work of Laporte and Lang. The values obtained in this work and given in Table III are in good agreement with the term values.

Some lines have been taken from a catalogue of unclassified Zinc lines published by L. et E. Bloch (*Jour. de Phys. et le Rad.*, July, 1934); the letter 'B' has been written behind them. The letter 'K' indicates that the lines have been taken from Kayser's *Handbuch*, vol. 6, pp. 858–60.

TABLE

		$3d^{10}$	$3d^9 4s$				$3d^9 5s$			
		$^1S_0$ 324405	78105 $^3D_3$ 246300	1178 $^3D_2$ 245122	1576 $^3D_1$ 243546	2650 $^1D_2$ 240896	$^3D_3$ 109520	462 $^3D_2$ 109058	2322 $^3D_1$ 106736	185 $^1D_2$ 106551
			9	6	3	4	3			1
186529	$^3P_2$		59771	58593	57016	54366	77010	†	†	79976
2204										
		3		10	7	7		1	1	1
184325	$^3P_1$	140080		60797	59221	56569		75269	77587	77774
1321										
					8				1	
183004	$^3P_0$				60542				76268	
			15				3			
183070	$^3F_4$		63230				73550			
671										
			8	10		9	2	4		
183741	$^3F_3$		62558	61381		57154	74222	74684		*
1827			5	10		3	0	2	4	2
181914	$^3F_2$		64387 (1)	63208	61633	58981	72396	72857	75178	75363
			8	1		10	4	2		4
179894	$^3D_3$		66403	65226 (2)		61002	70377	70838		73345
741			2	8	6	8	0	3	1	2
179153	$^3D_2$		67144	65969	64396 (1)	61744	69632	70097	72418	72601
2253		6		4	6	9			3	2
176900	$^3D_1$	147504 (3)		68222	66646	63998		†	70165	70348
		6		5	5	7 + C		3		3
176828	$^1P_1$	147576 (4)		68294	66718	64068		67768	2	70275
351			5	8	7	7	1	0		3
176477	$^1D_2$		69821	68645	67068	64419	66954	67417	69742	69925
−1954			8	6		9	3	2		2
178431	$^1F_3$		67869	66689		62468	68909	69373		71881

.ted in the present investigation. (2) Located and measured in the present investigation.
(3) and (4) Measurement obtained in the present investigation.
† Missing satellites. * Missing intercombinations.

TABLE III.—THE TERM VALUES OF ZnIII

Terms	Values	Terms	Values
$3d^{10}\ {}^1S_0$	324405 cm.$^{-1}$	$3d^9 4d\ {}^1F_3$	105053 cm.$^{-1}$
		,, ${}^1G_4$	109284
$3d^9 4s\ {}^3D_3$	246300		
.. ${}^3D_3$	245122	$3d^8 4s 4p(^4F)\ {}^5D_4$	72094
,, ${}^3D_1$	243546	,, ${}^5D_3$	70273
,, ${}^1D_2$	240896	,, ${}^5D_2$	70666
		,, ${}^5D_1$	68958
$3d^9 4p\ {}^3P_2$	186529	,, ${}^5D_0$	66333
,, ${}^3P_1$	184325	${}^5F_5$	?
,, ${}^3P_0$	183004	${}^5F_4$	72118
,, ${}^3F_4$	183070	${}^5F_3$	71990
,, ${}^3F_3$	183741	,, ${}^5F_2$	70702
${}^3F_2$	181914 ,,	,, ${}^5F_1$	68770
${}^3D_3$	179894 ,,	,, ${}^5G_6$	?
${}^3D_2$	179153 ,,	${}^5G_5$	?
${}^3D_1$	176900	${}^5G_4$	72376
${}^1P_1$	176828	${}^5G_3$	71825
,, ${}^1D_2$	176477	${}^5G_2$	68104
,, ${}^1F_3$	178431	${}^3D_3$	58913
		${}^3D_2$	54402
$3d^9 5s\ {}^3D_3$	109520	${}^3D_1$	52301
,, ${}^3D_2$	109058	${}^3F_4$	58867
,, ${}^3D_1$	106736	${}^3F_3$	58444
,, ${}^1D_2$	106551	${}^3F_2$	52269
		${}^3G_5$	?
$3d^9 4d\ {}^3S_1$	110043	${}^3G_4$	60576
,, ${}^3P_2$	106741	${}^3G_3$	60882
,, ${}^3P_1$	105487		
,, ${}^3P_0$	103042		
,, ${}^3D_3$	106357	$3d^8 4s 4p(^2F)\ {}^3D_3$	48277
,, ${}^3D_2$	105857	.. ${}^3D_2$	46166
,, ${}^3D_1$	103055	${}^3D_1$	44189
,, ${}^3F_4$	105037	${}^3F_4$	46266
,, ${}^3F_3$	104713	${}^3F_3$	47081
,, ${}^3F_2$	103731	${}^3F_2$	46437
,, ${}^3G_5$	107788	${}^3G_5$	?
,, ${}^3G_4$	107932	${}^3G_4$	50251
,, ${}^3G_3$	107323	${}^3G_3$	49138
,, ${}^1S_0$	108929	${}^1D_2$	50066
,, ${}^1P_1$	103073	${}^1F_3$	47657
,, ${}^1D_2$	107502	${}^1G_4$	46801

TABLE IV.—CATALOGUE OF DOUBLY-IONISED ZINC LINES.

	λ	ν	Int.	Classification
B	3133·45	31904	2	$3d^9 4d\ {}^3F_2 - 3d^8 4s 4p\ {}^5G_3$
B	3091·69	32335	2	,, $^3F_3$ — ,, $^5G_4$
B	60·68	32663	2	,, $^3F_4$ — ,, $^5G_4$
B	55·06 (Cd?)	32723	2	,, $^3F_2$ — ,, $^5F_3$
B	39·82	32887	1	,, $^3F_3$ — ,, $^5G_3$
B	35·13	32938	3	, $^1F_3$ — , $^5F_4$
B	25·31	33045	1	,, $^3F_4$ — ,, $^5F_3$
B	24·70	33059 ?	1	,, $^1F_3$ — ,, $^5F_3$
B	2942·12	33979	3	, $^3D_3$ — ,, $^5G_4$
B	16·24	34281	2	,, $^3D_1$ — ,, $^5F_1$
B	2875·94	34761	4	, $^3F_4$ — ,, $^5D_3$
B	60·07	34954	0	,, $^3D_1$ — ,, $^5G_2$
B	39·41	35208	2	,, $^3G_3$ — ,, $^5F_4$
B	37·47	35232	4	,, $^3G_3$ — ,, $^5D_4$
B	29·54	35331	0	,, $^3G_3$ — ,, $^5F_3$
B	2786·00	35883	1	$3d^9 5s\ {}^1D_2$ — ,, $^5D_2$
B	68·52	36109 II?	1	$3d^9 4d\ {}^3G_4$ — ,, $^5G_3$
B	20·83	36742	5	,, $^1P_1$ — ,, $^5D_0$
B	09·44	36897 IV?	3	,, $^3D_2$ — ,, $^5D_1$
B	2695·84	37083	3	,, $^3D_2$ — ,, $^5F_1$
B	89·64	37168 IV?	0	,, $^1G_4$ — ,, $^5F_4$
B	87·82	37193 IV?	1	,, $^1G_4$ — ,, $^5D_4$
B	84·97	37233 IV?	0	$3d^9 5s\ {}^5D_2$ — ,, $^5G_3$
B	59·51	37590 IV?	3	,, $^1D_2$ — ,, $^5D_1$
B	04·18	38388	1	,, $^3D_2$ — ,, $^5D_2$
B	2593·83	38542	1	$3d^9 4d\ {}^1D_2$ — ,, $^5D_1$
B	2265·05	44136 II?	2	,, $^3F_3$ — ,, $^3G_4$
K	2144·44	46618 II ?	1	,, $^1D_2$ — ,, $^3G_3$
K	38·59	46745	2	,, $^3G_4$ — ,, $^3G_4$
	2086·54	47911	0	,, $^3D_3$ — ,, $^3F_3$
K	39·33	49020	1	,, $^3G_4$ — ,, $^3D_3$
	1974·81	50638 ?	0	,, $^3D_3$ — ,, $^3F_3$
	68·92	50789	0	,, $^3D_1$ — ,, $^3F_2$
L	1839·40	54366	4	$3d^9 4s\ {}^1D_2 - 3d^9 4p\ {}^3P_2$
L	1767·75	56569	7	,, $^1D_2$ — ,, $^3P_1$
L	53·90	57016	3	,, $^3D_1$ — ,, $^3P_2$
L	49·66	57164	9	,, $^1D_2$ — ,, $^3F_3$
	47·68	57219	1	$3d^9 4d\ {}^3D_3 - 3d^8 4s 4p\ {}^3G_3$
	21·95	58074	1	,, $^3D_3$ — ,, $^3D_3$
L	06·67	58593	6	$3d^9 4s\ {}^3D_2 - 3d^9 4p\ {}^3P_0$
L	1695·46	58981	3	,, $^1D_2$ — ,, $^3F_2$
L	88·60	59221	7	,, $^3D_1$ — ,, $^3P_1$
L	73·05	59771	9	,, $^3D_3$ — ,, $^3P_2$
	58·25	60305	1	$3d^9 4d\ {}^3P_2 - 3d^8 4s 4p\ {}^3F_2$
L	51·74	60542	8	$3d^9 4s\ {}^3D_1 - 3d^9 4p\ {}^3P_0$
L	44·81	60797	10	,, $^3D_2$ — ,, $^3P_1$
L	39·28	61002	10	,, $^1D_2$ — ,, $^3D_3$
L	29·17	61381	10	,, $^3D_2$ — ,, $^3F_3$
L	22·50	61633	10	,, $^3D_1$ — ,, $^3F_2$
L	19·59	61744	8	,, $^1D_2$ — ,, $^3D_2$
	01·62	62437	1	$3d^9 5s\ {}^3D_3 - 3d^8 4s 4p\ {}^3F_3$

TABLE IV (*continued*)

L	00·83	62468	9	$3d^9 4s\ ^1D_2 - 3d^9 4p\ ^1F_3$
	1598·91	62543	1	$3d^9 5s\ ^3D_1 - 3d^8 4s 4p\ ^3D_1$
L	98·51	62558	8	$3d^9 4s\ ^3D_3 - 3d^9 4p\ ^3F_3$
	95·07	62693	2	$3d^9 4d\ ^3P_2 - 3d^8 4s 4p\ ^1F_3$
	90·01	62889	1	$3d^9 5s\ ^3D_2$ — ,, $^3D_2$
L	82·09	63208	10	$3d^9 4s\ ^3D_2 - 3d^9 4p\ ^3F_2$
L	81·54	63230	15	$3d^9 4s\ ^3D_3$ — ,, $^3F_4$
	79·42	63315	0	$3d^9 4d\ ^1D_2 - 3d^8 4s 4p\ ^3D_1$
	1578·46	63353	0	$3d^9 5s\ ^3D_3 - 3d^8 4s 4p\ ^3D_2$
	65·63	63872	0	$3d^9 4d\ ^3S_1$ — ,, $^3D_2$
L	62·54	63998	9	$3d^9 4s\ ^1D_2 - 3d^9 4p\ ^3D_1$
L	60·83	64068	7+C	,, $^1D_2$ — ,, $^1P_1$
ML	53·12	64387	3	,, $^3D_3$ — ,, $^3F_2$
ML	52·87	64397	6	,, $^3D_1$ — ,, $^3D_2$
L	52·34	64419	7	,, $^1D_2$ — ,, $^1D_2$
	41·71	64863	1	$3d^9 5s\ ^3D_2 - 3d^8 4s 4p\ ^3D_1$
ML	33·15	65225	1	$3d^9 4s\ ^3D_2 - 3d^9 4p\ ^3D_3$
L	15·84	65959	8	,, $^3D_2$ — ,, $^3D_2$
L	05·95	66403	8	,, $^3D_3$ — ,, $^3D_3$
	05·335	66430	1	,, $^1D_2 - 3d^9 4d\ ^3S_1$
L	00·47	66646	6	,, $^3D_1 - 3d^9 4p\ ^3D_1$
L	1499·49	66689	6	,, $^3D_2$ — ,, $^1F_3$
L	98·84	66718	5	,, $^3D_1$ — ,, $^1P_1$
	97·43	66782	2	$3d^9 4p\ ^1P_1 - 3d^9 4d\ ^3S_1$
	93·56	66954	1	,, $^1D_2 - 3d^9 5s\ ^3D_3$
L	91·02	67068	7	$3d^9 4s\ ^3D_1 - 3d^9 4p\ ^1D_2$
L	89·33	67144	2	,, $^3D_3$ — ,, $^3D_2$
	83·305	67417	0	$3d^9 4p\ ^1D_2 - 3d^9 5s\ ^3D_2$
	75·631	67768	3	,, $^1P_1$ — ,, $^3D_2$
L	73·43	67869	8	$3d^9 4s\ ^3D_3 - 3d^9 4p\ ^1F_3$
	72·767	67899	1	$3d^9 4p\ ^1P_1 - 3d^9 4d\ ^1S_0$
	71·243	67970	1	,, $^3D_1$ — ,, $^1S_0$
L	65·80	68222	4	$3d^9 4s\ ^3D_2 - 3d^9 4p\ ^3D_1$
L	64·26	68294	5	,, $^3D_2$ — ,, $^1P_1$
L	56·77	68645	8	,, $^3D_2$ — ,, $^1D_2$
	51·182	68909	3	$3d^9 4p\ ^1F_3 - 3d^9 5s\ ^3D_3$
	49·788	68976	0	,, $^1D_2 - 3d^9 4d\ ^1D_2$
	46·927	69112	0	,, $^3D_2$ — ,, $^3S_1$
	46·266	69146	0	,, $^1F_3$ — ,, $^1G_4$
	1446·088	69152		$3d^9 4p\ ^1D_2 - 3d^9 4d\ ^3G_3$
	42·487	69325		,, $^1P_1$ — ,, $^1D_2$
	41·492	69373		,, $^1F_3 - 3d^9 5s\ ^3D_2$
	36·118	69632	0	,, $^3D_2$ — ,, $^3D_3$
	33·847	69742	2	,, $^1D_2$ — ,, $^3D_1$
L	32·23	69821	5	$3d^9 4s\ ^3D_3 - 3d^9 4p\ ^1D_2$
	30·108	69925	3	$3d^9 4p\ ^1D_2 - 3d^9 5s\ ^1D_2$
	26·590	70097	3	,, $^3D_2$ — ,, $^3D_2$
	25·220	70165	3	,, $^3D_1$ — ,, $^3D_1$
	22·976	70275	3	$^1P_1$ — ,, $^1D_2$
	21·500	70348	2	$^3D_1$ — ,, $^1D_2$
	20·923	70377	4	$^3D_3$ — ,, $^3D_3$

TABLE IV (*continued*)

λ	ν	Int.	Classification
16·234	70610	1	$3d^9 4p\ {}^3D_3 - 3d^9 4d\ {}^1G_4$
16·070	70618	0	,, ${}^1D_2$ — ,, ${}^3D_2$
11·665	70838	2	,, ${}^3D_3 - 3d^9 5s\ {}^3D_3$
09·863	70929	1	,, ${}^1F_3 - 3d^9 4d\ {}^1D_2$
08·675	70989	2	,, ${}^1D_2$ — ,, ${}^3P_1$
(Mixed) 07·620	71042	?	,, ${}^3D_1$ — ,, ${}^3D_2$
06·311	71108	4	,, ${}^1F_3$ — ,, ${}^3G_3$
01·755	71339	2	,, ${}^1P_1$ — ,, ${}^3P_1$
1395·624	71653	3	,, ${}^3D_2$ — ,, ${}^1D_2$
94·902	71690	4	,, ${}^1F_3$ — ,, ${}^3P_2$
93·448	71764	1	,, ${}^1D_2$ — ,, ${}^3F_3$
92·143	71832	0	,, ${}^3D_2$ — ,, ${}^3G_3$
91·182	71881	2	,, ${}^1F_3 - 3d^9 5s\ {}^1D_2$
89·590	71964	4	,, ${}^3D_3 - 3d^9 4d\ {}^3G_4$
87·468	72074	3	,, ${}^1F_3$ — ,, ${}^3D_3$
81·310	72396	00	,, ${}^3F_2 - 3d^9 5s\ {}^3D_3$
81·009	72411	1	,, ${}^3D_2 - 3d^9 4d\ {}^3P_2$
80·873	72418	1	,, ${}^3D_2 - 3d^9 5s\ {}^3D_1$
77·941	72572	3	,, ${}^1F_3 - 3d^9 4d\ {}^3D_2$
,,	,,	,,	,, ${}^3D_2$ — ,, ${}^3G_3$
1377·394	72601	2	,, ${}^3D_2 - 3d^9 5s\ {}^1D_2$
74·647	72746	3	,, ${}^1D_2 - 3d^9 4d\ {}^3F_2$
73·705	72796	4	,, ${}^3D_2$ — ,, ${}^3D_3$
72·554	72857	2	,, ${}^3F_2 - 3d^9 5s\ {}^3D_2$
70·529	72965	1	,, ${}^3P_0 - 3d^9 4d\ {}^3S_1$
68·088	73095	4	,, ${}^1P_1$ — ,, ${}^3F_2$
66·991	73153	4	,, ${}^3D_3$ — ,, ${}^3P_2$
66·698	73169	3	,, ${}^3D_1$ — ,, ${}^3F_2$
65·685	73223	5	,, ${}^1D_2$ — ,, ${}^1F_3$
64·346	73295	4	,, ${}^3D_2$ — ,, ${}^3D_2$
63·400	73346	4	,, ${}^3D_3 - 3d^9 5s\ {}^1D_2$
62·524	73393	3	,, ${}^1F_3 - 3d^9 4a\ {}^3F_4$
62·010	73421	4	,, ${}^1D_2$ — ,, ${}^3D_1$
59·823	73558	4	,, ${}^3D_3$ — ,, ${}^3D_3$
59·618	73550	3	,, ${}^3F_4 - 3d^9 5s\ {}^3D_3$
56·530	73718	2	,, ${}^1F_3 - 3d^9 4d\ {}^3F_3$
55·931	73750	3	,, ${}^1P_1$ — ,, ${}^1P_1$
55·490	73774	0	,, ${}^1P_1$ — ,, ${}^3D_1$
55·250 II?	73787	3	,, ${}^1P_1$ — ,, ${}^3P_0$
,,	,,	,,	,, ${}^3F_4$ — ,, ${}^1G_4$
54·193	73845	2	,, ${}^3D_1$ — ,, ${}^3D_1$
53·947	73858	2	,, ${}^3D_1$ — ,, ${}^3P_0$
50·651	74038	2	,, ${}^3D_3$ — ,, ${}^3D_2$
47·302	74222	2	,, ${}^3F_3 - 3d^9 5s\ {}^3D_3$
46·161	74285	3	,, ${}^3P_1 - 3d^9 4d\ {}^3S_1$
43·338	74441	4	,, ${}^3D_2$ — ,, ${}^3F_3$
38·968	74684	4	,, ${}^3F_3$ — ,, ${}^3D_2$
(Mixed) 38·652	74702	0	,, ${}^1F_3 - 3d^9 4a\ {}^3F_2$
35·843	74859	2	,, ${}^3D_3$ — ,, ${}^3F_4$
30·924	75136	3	,, ${}^3F_4$ — ,, ${}^3G_4$
30·170	75178	4	,, ${}^3F_2 - 3d^9 5s\ {}^3D_1$

TABLE IV (*continued*)

λ	ν	Int.	Classification
1330·170	75178	4	$3d^9 4p\ {}^1F_3 - 3d^9 4d\ {}^1F_3$
28·561	75269	1	,, $^3P_1 - 3d^9 5s\ {}^3D_2$
28·340	75282	5	,, $^3F_4 - 3d^9 4d\ {}^3G_5$
26·910	75363	2	,, $^3F_2 - 3d^9 5s\ {}^1D_2$
26·290	75398	0	,, $^3P_1 - 3d^9 4d\ {}^1S_0$
25·891	75421	1	,, $^3D_2$ — ,, $^3F_2$
23·515	75556	3	,, $^3F_2$ — ,, $^3D_3$
19·135	75807	5	,, $^3F_3$ — ,, $^3G_4$
14·840	76055	1	,, $^3F_2$ — ,, $^3D_2$
14·118	76097	2	,, $^3D_2$ — ,, $^3D_1$
12·984	76162	1	,, $^3D_3$ — ,, $^3F_2$
11·169	76268	1	,, $^3P_0 - 3d^9 5s\ {}^3D_1$
08·610	76417	1	,, $^3F_3 - 3d^9 4d\ {}^3G_3$
07·414	76487	3	,, $^3P_2$ — ,, $^3S_1$
04·787	76641	3	,, $^3D_3$ — ,, $^1F_3$
03·565	76713	5	,, $^3F_4$ — ,, $^3D_3$
01·697	76823	2	,, $^3P_1$ — ,, $^1D_2$
1298·709	77000	1	,, $^3F_3$ — ,, $^3P_2$
98·540	77010	3	,, $^3P_2 - 3d^9 5s\ {}^3D_3$
95·321	77201	4	,, $^3F_2 - 3d^9 4a\ {}^3F_3$
92·232	77386	4	,, $^3F_3$ — ,, $^3D_3$
90·016	77518	2	,, $^3P_0$ — ,, $^3P_1$
88·875	77587	1	,, $^3P_1 - 3d^9 5s\ {}^3D_1$
85·781	77774	1	,, $^3P_1$ — ,, $^1D_2$
83·937	77885	2	,, $^3F_3 - 3d^9 4d\ {}^3D_2$
81·525	78032	3	,, $^3F_4$ — ,, $^3F_4$
79·019	78185	2	,, $^3F_2$ — ,, $^3F_2$
76·217	78357	3	,, $^3F_4$ — ,, $^3F_3$
74·370	78470	4	,, $^3P_1$ — ,, $^3D_2$
1270·549	78706	3	,, $^3F_3$ — ,, $^3F_4$
68·386	78840	3	,, $^3P_1$ — ,, $^3P_1$
,,	,,	,,	,, $^3F_2$ — ,, $^1P_1$
68·044	78861	3	,, $^3F_2$ — ,, $^3D_1$
65·396	79027	3	,, $^3P_2$ — ,, $^1D_2$
,,	,,	,,	,, $^3F_2$ — ,, $^3F_3$
62·515	79207	5	,, $^3P_2$ — ,, $^3G_3$
53·322	79788	5	,, $^3P_2$ — ,, $^3P_2$
51·024	79935	2	,, $^3P_0$ — ,, $^1P_1$
50·375	79976	1	,, $^3P_2 - 3d^9 5s\ {}^1D_2$
47·375 (C)	80170	1	,, $^3P_2 - 3d^9 4d\ {}^3D_3$
42·409	80489	1	,, $^3F_3$ — ,, $^1F_3$
40·757	80596	1	,, $^3P_1$ — ,, $^3F_2$
39·603 (IV?)	80671	1	,, $^3P_2$ — ,, $^3D_2$
33·928	81042	2	,, $^3P_2$ — ,, $^3P_1$
30·434	81272	1	,, $^3P_1$ — ,, $^3D_1$
30·296	81281	0	,, $^3P_1$ — ,, $^3P_0$
00·842	83275	1	,, $^3P_2$ — ,, $^1F_3$
L 713·88	140080	3	$3d^{10}\ {}^1S_0 - 3d^9 4p\ {}^3P_1$
ML 677·948	147504	6	$3d^{10}\ {}^1S_0$ — ,, $^3D_1$
ML 677·615	147576	6	$3d^{10}\ {}^1S_0$ — ,, $^1P_1$

TABLE IV (*continued*)

		Int.	Classification		
591·474	169069		$3d^9 4s$ $^1D_2$ —	$3d^8 4s 4p(^4F)$	$^5G_3$
86·090	170622		,, $^1D_2$ —	,,	$^5D_2$
82·907	171554		,, $^3D_1$ —	,,	$^5F_3$
(Mixed) 80·976	172124		,, $^1D_2$ —	,,	$^5F_1$
78·558	172844		,, $^3D_1$ —	,,	$^5F_2$
77·586	173134		,, $^3D_2$ —	,,	$^5F_3$
77·037	173299		,, $^3D_2$ —	,,	$^5G_2$
74·964	173924		,, $^3D_3$ —	,,	$^5G_4$
74·114	174182		,, $^3D_3$ —	,,	$^5F_4$
74·034	174206		,, $^3D_3$ —	,,	$^5D_4$
73·686	174311		,, $^3D_3$ —	,,	$^5F_3$
73·326	174421		,, $^3D_2$ —	,,	$^5F_2$
72·211	174456		,, $^3D_2$ —	,,	$^5D_2$
73·151 ?	174474		,, $^3D_3$ —	,,	$^5G_3$
72·778	174588		,, $^3D_1$ —	,,	$^5D_1$
72·154	174778		,, $^3D_1$ —	,,	$^5F_1$
71·915	174851	2	,, $^3D_2$ —	,,	$^5D_3$
69·989	175442		,, $^3D_1$ —	,,	$^5G_2$
68·098	176026	3	,, $^3D_3$ —	,,	$^5D_4$
64·294	177213	1	,, $^3D_1$ —	,,	$^5D_0$
549·505	181982	1	$^1D_2$ —	,,	$^3D_3$
42·770	184240	2	$^3D_2$ —	,,	$^3G_3$
39·170	185490	1	$^3D_3$ —	,,	$^3G_3$
38·433	185724	2	$^3D_3$ —	,,	$^3G_4$
37·031	186209	2	$^3D_2$ —	,,	$^3D_3$
35·533	186680	1	,, $^3D_2$ —	,,	$^3F_3$
33·652	187388		$^3D_3$ —	,,	$^3D_3$
33·525	187433		$^3D_3$ —	,,	$^3F_4$
32·317	187855		$^3D_3$ —	,,	$^3F_3$
528·099	189140		$^3D_1$ —	,,	$^3D_2$
24·334	190718	2	$^3D_2$ —	,,	$^3D_2$
22·892	191244		$^3D_1$ —	,,	$^3D_1$
22·646 ?	191280		$^3D_1$ —	,,	$^3F_2$
21·100	191902		$^3D_3$ —	,,	$^3D_2$
18·609	192823	1	$^3D_2$ —	,,	$^3F_2$
19·016 ?	192619		$^1D_2$ —	$3d^8 4s 4p(^2F)$	$^3D_3$
17·355	193237		$^1D_2$ —	,,	$^1F_3$
16·844	193482		$^3D_1$ —		
15·813	193815				$^3F_3$
14·244	194460		$^1D_2$ —	,,	$^3F_2$
13·543	194726		$^1D_2$ —	,,	$^3D_2$
12·678	195054		$^3D_2$ —	,,	$^1D_2$
10·244	195985		$^3D_2$ —	,,	$^3G_3$
10·078	196049		$^3D_3$ —	,,	$^3G_4$
08·013	196845		$^3D_2$ —	,,	$^3D_3$
(Mixed) 07·338	197107		$^3D_1$ —	,,	$^3F_2$
07·197	197162		$^3D_3$ —	,,	$^3G_3$
06·639	197379		$^3D_1$ —	,,	$^3D_2$
04·996	198021		$^3D_3$ —	,,	$^3D_3$

TABLE IV (*continued*)

λ	ν	Int.	Classification
04·946	198041	2	$3d^9 4s\ ^3D_2 - 3d^8 4s4p(^2F)\ ^3F_3$
03·410	198645	2	,, $^3D_3$ — ,, $^1F_3$
02·623	198956	2	,, $^3D_2$ — ,, $^3D_2$
01·620	199354	1	,, $^3D_1$ — ,, $^3D_1$
01·255	199499	3	,, $^3D_3$ — ,, $^1G_4$
499·914	200034	3	,, $^3D_3$ — ,, $^3F_4$
99·673	200131	1	,, $^3D_3$ — ,, $^3D_3$
99·669	200936	1	,, $^3D_2$ — ,, $^3D_1$

SUMMARY

An exhaustive experimental investigation of the spark spectrum of Zinc has been carried out, the range covered extending from λ 2600 to 400A. The lines corresponding to different stages of ionisation have been sorted out by introducing inductance in the spark circuit. *Two hundred and twenty-two* (222) *new lines of ZnIII have been classified, identifying fifty-three* (53) *new terms which consist of* $3d^9 5s$, $3d^9 4d$ *and a part of* $3d^8 4s4p$. **The term values** have been calculated by means of the $4s - 4p$ and $4p - 5s$ groups of lines. The value obtained for the deepest term $3d^{10}\ ^1S_0$ is 324405 cm.$^{-1}$, which corresponds to an ionisation potential of about 40 volts.

In conclusion the writer wishes to express his deep sense of gratitude to Prof. A. Fowler, F.R.S., for the help in working out the analysis, to Prof. M. Siegbahn for permitting him to work in the Fysicum of the Upsala University, and to Sir J. C. Bose, F.R.S., for his kind help and encouragement to pursue the work in the Bose Research Institute.

XII.—ABSORPTION SPECTRA OF THE ALKALI HALIDES AND THEIR CONSTITUENTS IN SOLUTION

BY

A. K. DUTTA, D.Sc.

THE absorption spectra of the alkali halides have drawn considerable attention for some time. Franck and his collaborators (1) have studied the absorption spectra of these substances in the vapour state. They have found two regions of continuous absorption in the case of the bromides and the iodides, and one region of absorption in the case of the chlorides. It has been put forward that the first absorption in the case of the chlorides, bromides and iodides indicates dissociation of the compounds into two normal atoms, and that the second absorption, obtained with the bromides and the iodides only, corresponds to dissociation into normal alkali atoms and excited halogen atoms in the $^2P_{\frac{1}{2}}$ state. The excitation energy for chlorine being very small, the second absorption is not observed with the chlorides.

Alkali halides, as a group of strong electrolytes, are not generally expected to preserve their compound identity in the state of solution, and as such are expected to give a different type of absorption spectra. A critical study of the absorption spectra of these compounds in solution is expected to throw some light on their condition in solution and thus help us in forming a proper estimate of the theory of dissociation of the strong electrolytes. The absorption spectra of the alkali halide solutions have been studied specially with this object in view.

EXPERIMENT

The alkali halides of reagent quality (Merck or Kahlbaum) have generally been used. Solutions were made in distilled

water, and the absorption spectra of a halide at different concentrations were taken. The maximum concentration used was 12 Normal in the case of lithium chloride. Generally, however, the saturated solutions of the different alkali halides were of much lower strength. The average maximum strength of the solutions was about 5 Normal. The spectra were taken at the maximum concentration, as also at weaker strengths; the limit of dilution used was N/1000. Fifteen cm. long glass tubes, with quartz windows, have been used as absorption chambers. A small quartz spectrograph of E_3 type was used.

It has been observed in the case of the chlorides that there are generally two regions of continuous absorption separated by a patch of transmitted light. With a very strong concentration it has sometimes been observed that the patch of retransmitted light vanishes away into the two superimposing absorption patches. It has further been observed that the absorption is quite negligible at a rather high concentration of about N/10 strength of the solution.

In the case of the alkali bromides two regions of continuous absorption have been observed with lithium bromide and rubidium bromide. The first region of absorption could not be traced in the case of the sodium and potassium bromides. The regions of second absorption were almost the same in all the four cases studied. The first region of absorption, wherever obtained, appeared only at high concentrations of about the Normal strength. Slight absorption prevailed even at higher dilutions.

TABLE I.—REGIONS OF ABSORPTION AND THE CORRESPONDING ENERGIES FOR THE ALKALI CHLORIDES

Substance	First region	Energy	Second region	Energy
LiCl	2760 Å	104 K	2350 Å	121 K
NaCl	2760 Å (faint)	,,	,,	,,
KCl	2760 Å (stronger than in NaCl)	,,	,,	,,
RbCl	3000 Å	95 K	—	—
CsCl	2800 Å	102 K	2350 Å	121 K

With the iodides studied, viz. lithium, sodium and potassium iodides, two regions of absorption have been found in each case. The first region of absorption is comparatively much weaker than the second region of absorption, and has been obtained with high concentrations only, as in the case of the bromides. It has been further observed that there is appreciable absorption in the second region at a very low dilution. The nature and the region of absorption in all the three iodides are similar.

The regions of absorption and the corresponding energy in kilo-calories are given in Tables I to III.

TABLE II.—REGIONS OF ABSORPTION AND THE CORRESPONDING ENERGIES FOR THE ALKALI BROMIDES

Substance	First region	Energy	Second region	Energy
LiBr	3000 Å	95 K	2550 Å	112 K
NaBr	—	—	,,	,,
KBr	—	—	,,	,,
RbBr	3000 Å	95 K	2600 Å	110 K

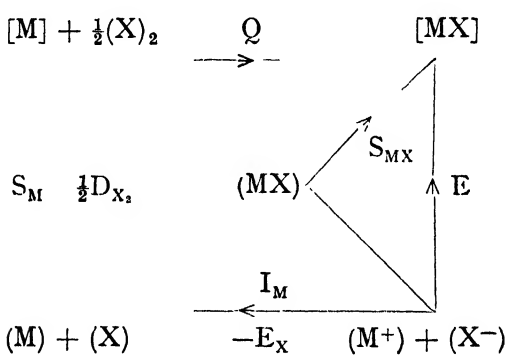
TABLE III.—REGIONS OF ABSORPTION AND THE CORRESPONDING ENERGIES FOR THE ALKALI IODIDES

Substance	First region	Energy	Second region	Energy
LiI	3500 Å	80 K	3000 Å	95 K
NaI	3600 Å	,,	2850 Å	100 K
KI	,,	,,	,,	,,

Some previous workers (2) had been attracted towards the spectra of the alkali halide solutions and had been content with the experimental results alone. Moreover, there is a conflict of opinion about the results obtained by the different workers. The general nature of the experimental findings

of some of these investigators agree with the results here obtained.

Scheibe (3) first tried to interpret the results on the lines of the explanations offered by Franck and his co-workers for the vapour state. Evidently since the vapour state deals with the case of an undissociated molecule, whereas a strong electrolyte in solution is supposed to be of dissociated components, a conclusion drawn on the lines of the alkali halide vapours would be based on erroneous supposition. A direct comparison of the positions of the absorption spectra in the vapour state and in the state of solution, as has been done by Butkow (4) in the case of the cadmium and lead halides, and a conclusion drawn from such direct comparison is open to some criticism. In the case of the mono-valent halides, for example, the energy of dissociation of the molecule in the vapour state from $(MX) \rightarrow M + X$ is obtained with the help of the Börn cycle shown below :



The energy of dissociation is given by the relation

$$D = Q + \tfrac{1}{2}D_{X_2} + S_M - S_{MX}.$$

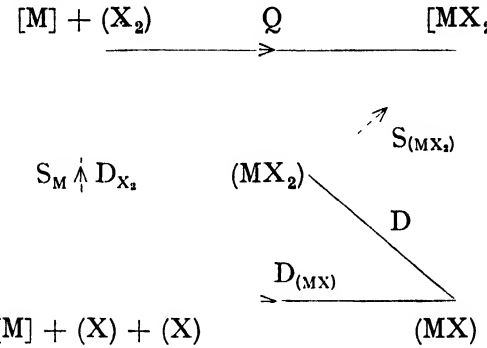
With di-valent halides, again, the reaction

$$(MX_2) \rightarrow (MX) + X$$

will involve the energy D, given by the expression

$$D = Q + S_M + D_{X_2} - S_{MX_2} - D_{MX}$$

as obtained from the modified Börn cycle shown below :



In the state of solution, evidently, an expression for the energy of dissociation will not involve the terms like S_M and S_{MX} or S_{MX_2} as the case may be, and even when we consider the substance to remain undissociated to a major extent, terms expressing the energy of solution and the energy of transformation from the solid and the gaseous states of the metal and the halogen to the respective atomic states in solution will make the whole expression quite complicated, some of the factors being yet unsolved. In the circumstances a direct comparison of the absorption regions in the vapour state and in the state of solution can lead us to no definite conclusion.

Franck and Scheibe (5) have interpreted the far ultra-violet absorption spectra of the alkali halide solution in the region of 2000 Å as an electron affinity spectrum of the halogen. They consider that the two maxima in the region are due to the electron affinity of the halogen atom in $^2p_{\frac{1}{2}}$ and $^2p_{\frac{3}{2}}$ states. The equation depicting the relation has been put forth as

$$h\nu = E_1 + H + P - S_1 - S$$

where ν is the frequency of the absorbed light,

E_1 is the electron affinity of the halogen atom,
H is the work of hydration of the halogen ion,
P is the potential energy of the water di-pole,
S is the heat of dilution of the halogen atom, and
S_1 is the electron affinity of water.

It has been further considered that the values of P and S are very small. With their experimental values of $h\nu$

and E and H, they have obtained the value of S_1 to be 18·5 K, which they considered to be a probable value.

Pauling (6), however, has pointed out that the electron affinity of water as obtained by Franck and Scheibe needs modification on two grounds and that theoretical consideration requires the long wavelength limit to be considered and not the position of the maximum in the absorption curve. Neglecting the small value of S, the proper form of the equation he considers to be :

$$E_X = h\nu + E_{H_2O} - 2H_X$$

in which E_{H_2O} has been written for S_1 in Franck and Scheibe's equation and P and H are considered equal. It has, further, been argued that the value of E_{H_2O} ought to be fairly high on the following considerations.

Bethe (7) has shown that the average potential in a liquid or a solid substance should be given by

$$V_O = \frac{2\pi eN}{3v} \sum_K \overline{r_K^2}$$

where $$\overline{r_K^2} = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r^2 \psi_K \psi_K^* r^2 \sin\theta \, dr \, d\theta \, d\varphi$$

r, θ, φ are the spatial polar co-ordinates of an electron in an atom relative to the nucleus and $\bar{r}_K^2$ is the average value of r^2 for the kth electron; N is Avogadro number, and V is the molar volume. Now the Pauli formula for the molar diamagnetic susceptibility is (8) :

$$\chi = -\frac{Ne^2}{6m_0c^2} \sum_K$$

so that V_0 becomes $$-\frac{4\pi m_0 c^2 \chi}{ev}$$

Putting k, the specific susceptibility for $\frac{\chi}{v}$ and writing the numerical value for the constants, one obtains

$$V_0 = -6{\cdot}43 \times 10^6 \sum K \text{ (in volts)}$$

and since the specific magnetic susceptibility of water is $-0{\cdot}72 \times 10^{-6}$

$$W_0 = eV_0 = 4{\cdot}63 \text{ (volt electrons)}.$$

W_0 is the average potential energy of the electron as it moves around in a medium. It has been shown by Pauling that the total energy of a free electron in the lowest state is expected to lie somewhere between $-W_0$ and $-\frac{1}{2}W_0$. In other words, the electron affinity E of the liquid should lie between $\frac{1}{2}W_0$ and W_0. This evidently agrees with the modified value of the electron affinity of water as obtained by Pauling's relation.

The values of the electron affinity of water E_{H_2O} in K.cal., as obtained by using the long wavelength limit of the ultra-violet absorption given in Tables I, II, and III are shown below for the respective cases of the chlorides, bromides and iodides. The values of E_X are those calculated by Born (9) and for H_X the values given by Webb (10) have been taken.

TABLE IV.—ELECTRON AFFINITY OF WATER AS OBTAINED BY PAULING'S RELATION

	E_X	$2H_X$	$h\nu$	E_{H_2O}
Cl^-	86	140	121	105
Br^-	86	132	112	106
I^-	79	122	95	106

The values of E_{H_2O} thus obtained tally with each other, and are just of the order expected according to Pauling's conjecture. The idea of Franck and Scheibe, that the far ultra-violet absorption spectrum of the alkali halide solutions is an electron affinity spectrum, is thus well supported; the values have, however, been modified.

As regards the first region of absorption in the case of the chlorides at about 2750Å, it has been, so far, very difficult to attribute any entity in the solution to be the absorbing centre. Fromherz and Menschick have tried to obviate the difficulty by explaining the absorption to be due to some impurities; particularly they consider that some inseparable grease traces have been responsible for the first absorption. But the fact must be admitted that the first region of absorption is persistent, as has been evident from the works of various earlier investigators also, and is fairly strong, so that it is unlikely that the absorption is due to

any impurity. It looks now as if the electron affinity of water might be the cause of the said absorption. As will be evident from a perusal of the Tables I and IV, the energy equivalents for the electron affinity of water and the first region of absorption with the chlorides agree remarkably well. According to this hypothesis, then, we are led to the conclusion that the halogens that are negatively ionised in the state of solution lose their electrons due to photo-electric process, and these become embedded into the free water molecules. The water molecules thus seem to have an affinity for the free electrons, and according to the measure of the electron affinity energy the binding force between the water molecules and the free electrons is quite large. It requires to be seen, however, whether the reverse process of reionisation of the halogens takes place automatically and whether some of the water molecules become ionised immediately the halide is dissolved. Experiments with this view are in project.

If the first absorption in the case of the chlorides is an electron affinity spectrum of the water molecules, it is naturally expected that such regions of absorption should occur with the bromides and the iodides also. But these regions of absorption are not observed with the latter compounds, perhaps due to the fact that with the requisite high concentration the iodides and some of the bromides show an absorption on a longer wavelength side. The only other alternative explanation of the first region of absorption with the chlorides might have been that some of the molecules remain undissociated at these concentrations and the absorption of light corresponds to dissociation of these molecules. But elaborate work on the electrolytic dissociation has shown that the chlorides become dissociated completely at all concentrations, and such an explanation thus becomes untenable. From all these considerations it seems plausible that the first region of absorption with the chlorides is an electron affinity spectrum although it requires to be better substantiated.

No satisfactory explanation has yet been offered for the first region of absorption in the case of the bromides and the iodides, nor has there been an attempt to explain them as due to any impurities. In the case of the iodides it had been suggested by Fromherz and Menschick that the absorption is due to I_3^- ion, as the absorption of I_3^- lies in the region (11).

But this fails in the case of the bromides as no such correspondence is found. It is further to be observed that such an entity as I_3^- is not expected to occur in the solution. Moreover, a significant point is that the first region of absorption is obtained only with high concentration of the salts and vanishes at a weaker dilution, and with some of the compounds like potassium bromide it could not be traced even at high concentrations. From the following discussion it seems plausible that the first absorption is due to the dissociation of the undissolved salt in solution.

Arrhenius first proposed the theory of ionic dissociation according to which an electrolyte dissociates into ions in solution and in many cases the dissociation is almost complete. He, however, considered that the degree of dissociation of the solute increases with dilution. The fraction of the salt that is ionised could be calculated from conductivity measurements on a simple hypothesis of ionic dissociation. But the change of conductivity of a strong electrolyte with concentration showed that the measurements of the conductivity on a basis of simple dissociation into ions could not explain the experimental facts completely in the case of the strong electrolytes, although it was quite successful in explaining the phenomenon with the weak electrolytes (12). To explain this anomaly diverse views were held, some considering the formation of complex ions to be responsible, while others thought that the equation connecting the degree of dissociation and the conductivity measurements needed some modification. It has been assumed that the change is mainly due to the electrostatic forces that exist between the ions. The general tendency of the deviation of the conductivity curve from the theoretical one is evidently expected from the interionic force. Milner's (13) calculations on this basis agreed with the osmotic pressure changes of salt solutions. Debye and Hückel (14) have made a detailed theoretical study of the conductivity of the strong electrolytes on the basis of interionic reaction. Their theoretical expressions have been so successful in explaining the trend of the conductivity measurement results that the hypothesis has been generally accepted. Debye and Hückel's equation, however, contains a term '*b*,' the mean ionic radius, which has not yet been accurately determined.

Onsager (15) has put in some important modifications in

Debye and Hückel's theory and his final expression does not contain any unknown term, so that the theory could be directly tested by comparison with experimental results. Both the equations of Debye and Hückel and of Onsager are based on the hypothesis of complete dissociation of the electrolyte. The Onsager equation has been thoroughly examined in the light of the experimental results and has been found to be quite satisfactory in dilute solutions. It remains, therefore, no longer a point of dispute that comparatively dilute solutions of electrolytes are completely ionised. With increased concentrations of the solution of the order of a normal strength, however, the deviation of the experimental results from the theoretical equation of Onsager becomes more and more prominent, particularly with some electrolytes. Increased viscosity in an ionised solution has been considered to be one of the causes of the deviation. Taking the viscosity factor into consideration, and comparing the theoretical values with the experimental results, Davies has pointed out that amongst the alkali halides, the alkali chlorides and potassium and sodium bromides show good agreement with the modified equation. In all these salts, therefore, the whole conductivity decrease can be attributed to the interionic force. But for the other salts examined, the experimental conductivity at the higher concentrations becomes in every case lower than the calculated values. This deviation, according to Davies (16), is presumably owing to incomplete dissociation and is corroborated by the dissociation constant values '*k*.'

The experimental results of the absorption spectra measurements of the alkali halide solutions lead us to the same conclusion. In the case of the chlorides, evidently no absorption patches due to dissociation of the undissolved molecules is expected, as the previous consideration shows that the salt is completely dissociated even at higher concentrations. It has, however, been possible to explain the absorption patches obtained with the chlorides and no region of absorption remains that could be attributed to the undissociated molecules.

With lithium bromide and lithium iodide the heats of formation of the salts in aqueous solution (17) are given in the following table, and this is compared with the experimental values of the absorption spectra and the corresponding energies.

TABLE V.—HEATS OF FORMATION OF THE LITHIUM BROMIDE AND LITHIUM IODIDE SALTS IN SOLUTION AND THE SPECTROSCOPICALLY OBTAINED ENERGIES

Equation of formation	Energy in k.cal.	Beginning of absorption	Energy in k.cal
$Li + Br_{fl} + aq. = LiBr.aq.$	95·4	3000 Å	95
$Li + I + aq. = LiI.aq.$	80·2	3500 Å	80

The comparison gives us the idea that the energy of absorption is spent in splitting up the compound in solution into the components with which it has been formed. Moreover, the first region of absorption appears only at high concentrations of about a normal strength, and from previous considerations undissociated molecules of LiBr and LiI are expected to occur in solution under the conditions. The agreement between the energy corresponding to the absorption edge and the thermochemical energy is thus supported by ideas of electrolytic dissociation.

The remarkable absence of the first region of absorption with KBr and NaBr, make the hypothesis of undissociated molecules more probable, since, as Davies has pointed out, molecules do not remain undissociated in the particular cases of KBr and NaBr even at the higher concentrations.

With NaI and KI, again, there are two regions of absorption as in the case of LiI. A direct comparison of the experimental results with the thermochemical values has not yet been possible, as the corresponding thermochemical values are not known. From a study of the other thermochemical data the values seem to be very probable, and it can be, so far, put forth that the first region of absorption wherever obtained with bromides and iodides denotes dissociation of the undissolved molecule into the constituents.

The absorption spectra of the alkali halide solution have thus been explained in detail. It appears from the above discussion that the chlorides become completely dissociated at all concentrations, forming negative halogen ions and positive alkali ions. With the requisite light energy the halogen ions lose their extra electron, which goes to form a negatively ionised water molecule. Excepting the salts

potassium bromide and sodium bromide, the other bromides and the iodides of the alkali metals remain undissociated to some extent at the higher concentrations of more than a normal strength. Complex ions and associated molecules in the state of solution have not been indicated by any absorption patches. The theory of associated water molecules of the type $(H_2O)n$ has been suggested by Rao (18) to occur in these solutions. If such entities are there, the energy of dissociation of these must lie in the red region or beyond.

It has not yet been possible, however, to explain completely the shifting of the absorption region towards the extreme ultraviolet with increased dilution or to account for the fact that the iodides show appreciable absorption at a dilution of N/1000 strength, whereas the bromides under the conditions absorb very slightly. These phenomena remain still to be explained.

Summary

The absorption spectra of the alkali halides in solution were studied in the ultraviolet region. Two regions of absorption were found with most of the compounds. The first region of absorption with the chlorides has been suggested to be the electron affinity spectrum of the water molecule. The idea of Franck and Scheibe, interpreting the second region as an electron affinity spectrum of the halogens, has been taken, but the values have been modified in the light of the present experimental results. The first region of absorption with the bromides and the iodides is considered to be due to the breaking up of the undissociated molecules that are present in the solution. This idea has been substantiated by evidences from the electrolytic dissociation theory.

My respectful thanks are due to Sir J. C. Bose, D.Sc., F.R.S., for his kind interest in the work and for all the facilities offered at the Bose Research Institute in carrying it out.

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XIII.—ABSORPTION SPECTRA OF ZINC AND CADMIUM HALIDES IN VAPOUR STATE

BY

SURESHCHANDRA DEB, D.Sc.

IN the case of compounds formed out of two partners with a bondage that is strictly heteropolar the energy of binding as obtained by chemical methods corresponds very well to that found from a study of the absorption spectrum in their gaseous state. The picture of the whole process is simple. The two reacting partners get charged in opposite senses; Coulomb's law immediately comes into operation between them and one gets the energy of attraction as

$$-A\frac{e}{r^2} \quad . \quad . \quad . \quad (1)$$

where e is the electronic charge and r is the distance between the centres of the two partners. By itself this attractive force would bring in difficulty, as this would lead to a coalition of the ions, *i.e.* the partners with opposite charges. So it is imagined, and not without justification, that at small distances repulsive forces come into play. The law governing the repulsion as given by quantum mechanics is

$$Be^{-r/\rho} \quad . \quad . \quad . \quad (2)$$

where B and ρ are constants. The position of equilibrium is then given by the value of r for which the sum of this part of the energy and the Coulomb energy has a minimum value. If by U we denote the mutual potential energy of the two ions, we may write :

$$U = -A\frac{e}{r} + Be^{-r/\rho} + D \quad . \quad . \quad (3)$$

D is a constant which is equivalent to the value of U when r tends to infinity. So that this represents the

energy of dissociation of the molecule into ions. This state of affairs exists when the molecule remains in its normal state.

It is assumed that by the action of light of suitable energy, $h\nu$, an electron is transferred from the ion with an excess of negative charge to that having an excess of the opposite charge. This leaves the partners electrically neutral, so that the Coulomb force previously existing between them vanishes. Now the energy relations between them take the form :

$$U' = B'e^{-r/\rho} + D'. \quad . \quad . \quad (4)$$

As a result the two partners, now the two neutral atoms, fly off from each other and the molecule gets dissociated, in this case not into ions but into atoms. If by M we denote the metal part of the molecule and by X the acid part, we can write :

$$M^+ X^- + h\nu = M + X \quad . \quad . \quad (5)$$

This energy $h\nu$ should be equivalent to the energy of formation of the molecule MX in its vapour state out of gaseous M and X atoms, a fact actually observed in experiments.

But difficulty arises when one takes up molecules with more than two partners, though chemically of the same type as the diatomic heteropolar ones.

Quite a good number of such molecules have been studied in absorption by various investigators in different laboratories. The characteristics of the spectra observed with them are very similar to the diatomic molecules, but practically none of them satisfies the energy relations that are expected to exist between the beginning of absorption and the binding energy of the molecule satisfactorily. We laid stress on this difficulty in a previous paper in these transactions when we reported our investigations on the lead halide vapours (1). It was found necessary to study many more similar cases before any definite conclusion could be arrived at. In this paper will be found our investigations on the vapours of zinc and cadmium di-halides in the visible and in the ultraviolet regions, and we are of opinion that so far as these compounds are concerned they behave more or less similar to the diatomic heteropolar compounds, a typical example of which is found in sodium chloride.

We are feeling a strong necessity to study the absorption of these molecules in the fluorite regions. But due to unavoidable reasons this part of our work at present remains incomplete. This we hope to investigate as soon as possible.

Zinc and cadmium atoms contain 2 electrons in an *s* shell, the total quantum number of which is 4 for zinc and 5 for cadmium, the inner electron shells '*s*,' '*p*' and '*d*' being previously filled. In this respect their resemblance to the alkali atoms is more pronounced than that of the alkaline earths, on account of the fact that the alkaline earth atoms possess a metastable *d*-level, whereas the alkalies and also Mg, Zn and Cd atoms do not possess these characteristics. While studying the absorption spectra of alkaline earth halides (2) we actually observed these metastable levels giving rise to an absorption band spectrum which was interfering with the general continuous absorption that arises from the heteropolarness of the molecules. As Zn and Cd atoms possess no such metastable levels it is expected that their absorption spectrum in the visible and in the ultraviolet regions should be free from any banded structure, a fact which will be helpful in the interpretation of the results.

Previous works on the absorption spectra of cadmium halides are by S. J. Evans (3). He took measured quantities of the salts in a sealed quartz tube, heated it inside an electric furnace and observed the spectrum due to the vapour in absorption. The object of his experiment was to ascertain whether these substances show the presence of well-defined absorption bands like vapours of iodine, bromine, selenium, etc.; on the contrary, he found that vapours of cadmium halides showed evidence of 'general selective absorption' in the ultraviolet. Though he experimented upon the vapours of mercury and cadmium halides and upon that of cadmium in its elementary state, he left the halides of zinc untouched. Recently K. Butkow (4), while studying in a general way the nature of binding in a triatomic molecule photochemically, included the iodides of zinc and cadmium in the list of molecules he undertook for his study. But the most important contribution on the nature of binding of heteropolar molecule having as one of its partners an element of the divalent group in the periodic table (Mg, Zn, Cd, Hg) next to the alkalies is by P. K. Sengupta (5). The salts he took for his experiments were the oxides and sulphides of

zinc, cadmium and mercury. Oxides and sulphides of zinc, cadmium and mercury, being themselves diatomic, are more similar to the diatomic alkali halides than the triatomic halides of those elements. And in interpreting the absorption spectra for a knowledge of the nature of the chemical binding that exists in the molecules Dr. Sengupta has further proved from his experiments that these oxides and sulphides behave very similar to the alkali halides. He showed, in the case of these oxides and sulphides, that the long wave limit of absorption due to the vapours of these salts corresponds with the thermochemical energy of the binding of these molecules, as is observed in the case of alkali halides. When oxides and sulphides behave in this way it is very unlikely that the halides of these elements, even if they be triatomic molecules, should behave otherwise.

To begin with, therefore, let us assume that when light is allowed to pass through the vapour of a molecule of the type MX_2, or more accurately $M^{++}\ 2(X^-)$, where M represents the metal and X the halogen part of the molecule, both of the extra electrons from $2(X^-)$ are simultaneously transferred to M^{++} and the molecule breaks up into three normal atoms. We represent the photochemical process of the dissociation as :

$$MX_2 + h\nu = M + 2X \quad . \quad . \quad (6)$$

There is a possibility that X may also get excited simultaneously during the process. If this happens we may write the above photochemical equation with a slight modification as :

$$MX_2 + h\nu' = M + 2X^* \quad . \quad . \quad (7)$$

where X^* is an excited halogen atom. As the normal state of M is an 1S-state without any metastable state near by, there is little possibility that M would also get excited in the process.

The above phenomena all arise out of a simultaneous transition of two electrons from X to the metal part M. But there is a likelihood of obtaining transitions in which the transference of only one electron is taking place. The resulting product of such a photochemical rearrangement can be written as :

$$MX_2 + h\nu_1 = MX + X \quad . \quad . \quad (8)$$

The next step in this process will be :

$$MX + h\nu_2 = M + X \quad . \quad . \quad (9)$$

so that

$$h\nu_1 + h\nu_2 = h\nu \quad . \quad . \quad (10)$$

Thus

$$\left.\begin{aligned} MX_2 + h\nu &= MX_2 + h\nu_1 + h\nu_2 \\ &= MX + X + h\nu_2 \\ &= M + X + X \end{aligned}\right\} \quad . \quad . \quad (11)$$

Apparatus and Experiments

The apparatus for the experiments consisted of three systems. (1) A source that gives continuous spectrum in the ultraviolet ; (2) a high-temperature furnace where the salts could be vaporised ; and (3) the photographing system. For (1) we used a hydrogen discharge tube run by a 4 K.W. transformer for the visible, violet and ultraviolet regions. The photographing system was a Leiss small quartz spectrograph for the ultraviolet part of the spectrum and for the visible a standard model constant deviation spectrograph by Fuess. For (2) a suitable furnace was designed, a description of which is given below.

Among the halides of zinc and cadmium $CdCl_2$ possesses the highest boiling point (954° C.). As there was no necessity for a higher temperature during our experiments a silica tube (internal diameter 1 inch and length 18 inches) was selected to contain the salt while vaporising. The tube was wound by nichrome wire (S.W.G. 24) about 10 inches at the middle. At each of the two ends of the tube two glass cone joints (female) were attached with sealing wax, a glass tube with a stop-cock having been previously sealed to each of the joints. To the corresponding male cones a transparent quartz piece was sealed. Thus the furnace had its quartz windows that could be taken out from it without disturbing any of the adjustments. The advantages of keeping the windows detachable are manifest in many directions. The furnace could be cleaned instantly whenever they got quoted. If any vapour comes and condenses on the cold part of the tube and thereby blocks the passage of the light from the hydrogen discharge tube it could be at once checked. The windows themselves being placed beyond the cones the possibility of their getting quoted with the condensed vapour of the substance from inside the

furnace is greatly reduced. And lastly, when cleaning the furnace to experiment with a fresh substance the necessity of breaking the sealings and resealing them afterwards is altogether avoided.

The furnace was calibrated with a thermocouple so that from the current passing through the heating coil the temperature inside the furnace could be ascertained.

Absorption spectra of the vapours of the substances were taken at different temperatures of the furnace. Photographs of absorption by the substance, from the time it remained still below its melting point through a number of states of intermediate temperatures to its state of boiling, were recorded on every negative. Before excitation all the air from inside the furnace was pumped out. It would have been better had we filled the furnace with nitrogen or with some inert gas. This would have prevented the diffusion of the vapour to the ends considerably and would have avoided the vapour of the iodides markedly from dissociation. But as we could not get the gas locally we had to do without it.

All the substances used in our experiments were chemically pure anhydrous samples obtained either from Kahlbaum's or from Merck's. Photographs were taken on Agfa Isochrome film for the ultraviolet and on Kodak Panatomic film for the visible and also for the ultraviolet part of the spectrum.

Copper arc was used for the comparison spectrum for all the regions.

Results

$ZnCl_2$.—The salt was very stable at quite high temperatures (900° C.). It melts at 290° C. and boils at 730° C. Between these limits eight exposures were given. At every fresh exposure the temperature of the furnace was raised approximately by 50° C., time of exposure being ten minutes for every exposure. Absorption was marked when the furnace was at 350° C., and at 500° C. the maximum wavelength limit of the absorption could be detected (λ 2600), which persisted even up to the highest temperature to which the furnace was raised. No other region of absorption was detected except the one noted above either in

the visible or in the ultraviolet, though it is expected that there may be some existing in the schumann region. The spectrum is strictly continuous.

$ZnBr_2$.—Melting and boiling points of zinc bromide are 390° C. and 695° C. respectively. In between these regions seven exposures for the absorption spectrum were given at temperature differences of approximately 50° C. Duration of exposure was ten minutes in each case. $ZnBr_2$ vapour was also fairly stable even at the highest temperature reached during the experiment (*c.* 700° C.). In this case also there was only one absorption region, the beginning of which was at λ 3100A. There was a trace of retransmission at the low temperatures, the beginning of which was at λ 2350, and as we intend to investigate the schumann and the fluorite regions thoroughly in future we leave at present anything concerning the region from which this retransmitted part is again absorbed. There was also a slight reduction of intensity at about λ 4000, but this might be due to traces of bromine that might be present from a slight decomposition of the salt.

ZnI_2.—This salt is not so stable as the corresponding chloride or bromide. There was a marked dissociation when the temperature was raised. The melting point of the salt is at about 250° C. and the boiling point, which is very uncertain, probably lies not very far from 620° C. The absorption spectrum observed was continuous, the beginning of which was at λ 3050A. There was also some continuous absorption in the blue region of the visible spectrum, the beginning of which was at about λ 4500A. This is the region for the band spectrum from the iodine molecule as well. But the bands that should possess an appearance of strong, sharp lines were weak and rather diffuse indicating the presence of the above-mentioned continuous absorption. The zinc line λ 3076A ($^1S - {}^3P$) was expected to appear particularly in the case of absorption due to iodide salt. But this could not be detected.

$CdCl_2$.—Behaves in a similar way to the corresponding compound with zinc and remains very stable all the time if vaporised in an anhydrous state. It melts at 568° C. and boils at 960° C. The absorption spectrum observed was perfectly continuous, began to appear at about the temperature of 650° C., and quickly reached the point of its

maximum wavelength limit, which lies at λ 2950A. This limit of absorption in the long wave side was quite sharply defined at higher temperatures. No other region of absorption could be located either in the quartz region or in the visible.

$CdBr_2$.—There was a tendency of this salt to get dissociated when vaporised, probably due to the presence of some moisture which could not be eliminated absolutely. The salt melts at 575° C. and boils at 800° C. As the salt could not be kept without being dissociated at higher temperatures no good photographs could be obtained with dense vapour. But at low temperatures, *i.e.* with low vapour pressure of the salt, good photographs were obtained in which the dissociation of the salt was not very much marked. The principal absorption was continuous, the long wavelength limit of which lies at about λ 3500. There were two other absorption regions, one at λ 4800 and the other at about λ 2300 A. The appearance of bromine bands was very much marked at high temperatures, though they were nearly absent at low ones. In the case of $CdBr_2$ absorption the time of exposure was 15 minutes in every case. The cadmium line λ 3251A could not be observed in absorption as it was probably within the region of absorption of $CdBr_2$ vapour.

CdI_2.—Melting and boiling points of cadmium iodide are 400° C. and 713° C. respectively. In our experiments we observed that the iodide of cadmium was more stable than the bromide salt of the same element. The absorption spectrum was continuous, the long wavelength limit of which was at λ 3600 A. At lower temperatures and with long exposures (20 minutes) there was located a region of retransmission which was again reabsorbed at about λ 2800. In the visible part of the spectrum there was a confusion between the absorption due to the iodine molecule, which was as usual very strong, and a continuous absorption due to the iodide, the region of which was probably at λ 5500 A. In this case also no cadmium line could be detected in the absorption.

In the following will be found (Table I) the results obtained in course of the above absorption experiments with the halides of zinc and cadmium summarised in tabular form. Wavelengths recorded in the table are those of the beginning of absorption in every case.

TABLE I.

Substance	1st region λ	2nd region λ	3rd region λ
$ZnCl_2$		2600	
$ZnBr_2$		3100	4000
ZnI_2	3050	4500	
	2650		
$CdCl_2$		2950	
$CdBr_2$	2300	3500	4800
CdI_2	3600	5500	
	2800		

THEORETICAL DISCUSSIONS

If by Q we denote the heat of formation of a molecule $[MX_2]$ (the molecule is considered to be in the state found in normal conditions, which is in the present case a solid state represented by square brackets) out of [M] and $[X_2]$ we write :

$$[M] + [X_2] = [MX_2] - Q \quad . \quad . \quad (12)$$

In order to get the heat of formation of an individual molecule MX_2 out of atomic M and atomic X we shall have to reduce [M] into M and $[X_2]$ into 2X as following :

$$[M] + L_M = M \quad . \quad . \quad . \quad (13)$$

where L_M represents the latent heat of vaporisation of the metal M, and

$$[X_2] + L_{X_2} = X_2 \quad . \quad . \quad (14)$$

and

$$X_2 + D_{X_2} = 2X \quad . \quad . \quad (15)$$

where L_{X_2} is the heat of vaporisation of X_2 from its solid state and D_{X_2} is its heat of dissociation. So that

$$M + L_M + 2X + L_{X_2} + D_{X_2} = MX_2 + L_{MX_2} - Q \quad (16)$$

where

$$[MX_2] = MX_2 - L_{MX}$$

L_{MX_2} being the latent heat of vaporisation of solid MX_2. Thus we get

$$M + 2X + Q + L_M + L_{X_2} + D_{X_2} - L_{MX_2} = MX_2 \quad (17)$$

If by ν we represent the frequency corresponding to the long wave limit λ of the absorption region, $h\nu$ will be the corresponding energy. Thus $h\nu$ is the energy of dissociation of the molecule found spectroscopically.

Thus we write :

$$MX_2 + h\nu = M + 2X \quad . \quad . \quad (18)$$

If R be the corresponding thermal unit of Kilo calories per mol we have :

$$MX_2 + R = M + 2X \quad . \quad . \quad (19)$$

Thus

$$R = \frac{Nh\nu}{J} \quad . \quad . \quad . \quad (20)$$

Comparing the relations (17) and (19) and taking into account the fact that Q is the energy of formation and R is that of dissociation

$$R = Q + L_M + L_{X_2} + D_{X_2} - L_{MX_2} \quad . \quad . \quad (21)$$

Thus with a knowledge of Q, L_M, L_{MX_2}, D_X, and L_{X_2} the value of R is known from purely thermochemical data. In the following will be found the available values for these quantities for the substances used in our experiments arranged in a tabular form.

TABLE II.—HEAT OF FORMATION OF ZN AND CD HALIDES IN K.CAL.

	Cl_2	Br_2	
Zn	97·2	75·93	49·23
Cd	93·24	76·3	48·33

TABLE III.—LATENT HEAT OF EVAPORATION OF THE METALS

Zn . . .	31·3 ± 0·70 k.cals.
Cd . . .	26·7 ± 0·75 k.cals.

TABLE IV.—LATENT HEAT OF VAPORISATION OF THE SALTS IN K.CAL.

	Cl_2	Br_2	I_2
Zn	33·2	27·6.	Not known
Cd	35·3	Not known	Not known

TABLE V.—HEAT OF DISSOCIATION OF HALOGENS

Cl_2	56·87 k.cal.
Br_2	45·2 k.cal.
I_2	35·5 k.cal.

It will be evident from the data given in Table IV that the heats of vaporisation of ZnI_2, $CdBr_2$ and CdI_2 are as yet unknown. A rough estimation of them is given below with the help of Trouton's rule. It is expected that these values, though not accurate, will not be very much wide from the true values.

Trouton's rule states :

$$L_{MX_2}/T = C \quad . \quad . \quad . \quad (22)$$

where T is the boiling point in absolute temperature and C is a constant. To determine the value of this constant C for the equation

$$\left(\frac{L}{T}\right)_{ZnI_2} = \quad (23)$$

we utilise the already determined values of the latent heat and the boiling point of zinc chloride. From p. 228 the value of T_{ZnCl_2} is 730° C., and from Table IV the value of L_{ZnCl_2} is 33210 calories per mol. Substituting these values in equation 22 above, we get :

$$C = \frac{33210}{(273 + 730)} = 33 \cdot 10$$

Utilising this value of C in equation (23) we get :

$$L_{ZnI_2} = C/(620 + 273) = 29 \cdot 5 \text{ k.cal.}$$

where the number 620 is the approximate boiling point of zinc chloride in ° Centigrade. The value of L_{ZnI_2} thus

estimated is certainly higher than the true value because the corresponding value for the zinc bromide as determined by Mr. M. S. Desai (6) is 27·6 k.cals. per mol. Still we accept it as a maximum limit.

To determine the latent heats of the salts $CdBr_2$ and CdI_2 we evaluate the constant C of equation (22) by utilising the known values of L_{CdCl_2} and T_{CdCl_2} which are 35300 calories and 960° C. respectively.

Thus for cadmium halides

$$C' = L_{CdCl_2}/T_{CdCl_2} = 35300/(273 + 960) = 28{\cdot}63 \quad (24)$$

Utilising this value of C′ we get

$$L_{CdBr_2} = (273 + 800) \times C' = 30{\cdot}7 \text{ k.cal.} \quad . \quad (25)$$

$$L_{CdI_2} = (273 + 713) \times C = 28{\cdot}2 \text{ k.cal.} \quad . \quad (26)$$

where 800 and 713 are the boiling points of $CdBr_2$ and CdI_2 respectively.

In Table VI the calculated values of ' R ' for all the substances as obtained with the help of the relation (21) are given. These are compared with the corresponding values of the beginnings of absorption as obtained in the course of the present investigation in columns 4 and 5 of the same table.

TABLE VI.

Substances	R		Beginning of absorption		Remarks
	k.cal.	λ	λ	k.cal.	
$ZnCl_2$	151·2	1880	—	—	Out of range of quartz region
$ZnBr_2$	124·8	2250	—	—	
ZnI_2	86·6	3330	3050	93·8	Diff. 24 k.cal.
			2650	108·0	$^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$ state of iodine atom
$CdCl_2$	141·8	2014	—	—	Out of range of instrument
$CdBr_2$	117·8	2440	2300	124	
CdI_2	72·7	3850	3600	80	Diff. 22 k. cal.
		2800	2800	102	$^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$ state of iodine atom.

From the above table it will be evident that in the case of cadmium and zinc iodides and also for cadmium bromide the beginning of absorption corresponds very well with the thermochemical energy of formation of the molecules out of two atoms of halogens and one of zinc or cadmium. In the case of ZnI_2 and CdI_2 we observed a retransmission of the continuous spectrum from the hydrogen discharge tube. This transmitted part was reabsorbed, the beginning of which lies at λ 2650 (108 k.cal.) for ZnI_2 and at λ 2800 (102 k.cal.) for CdI_2. This shows that the molecule is dissociating with one of the halogens getting excited. All these, especially the absorption phenomena of the retransmitted part of the background spectrum, as Prof. Frank asserts (7), strongly point to the direction that the chemical binding in the case of ZnI_2, CdI_2, and consequently for all the halides with these metals as well, is similar to that existing in the alkali halides.

One can imagine that while dissociating, instead of one of the halogens in the molecule MI_2, both of them get excited in the process. The effect of this would appear as a region of absorption in another portion of the transmitted part still further into the ultraviolet direction of the continuous spectrum. The excitation potential of iodine is 21·5 k.cal. (8). So that the position of this third region of reabsorption would lie at a position of the continuous spectrum the energy of which would be $(R + 2 \times 21{\cdot}5)$ k.cals. This is 130 k.cals. for ZnI_2 and 125 k.cals. for CdI_2. We searched for this retransmission and reabsorption but we could not observe them on our plates.

Explanation of other Absorption Regions

From Table I it will be found that there still remain other regions of absorption that await explanation. We find it difficult to put forward a consistent interpretation for these absorption regions absolutely free from objection. The best course for us, in the circumstances, would be to put forth all possible explanations for these and at the same time point out the difficulties in accepting them.

The most prominent absorption region other than that corresponding to the thermochemical energy R is reproduced below (Table VII) from Table I.

TABLE VII.

Substance	Beginning of absorption	
	λ	k.cals.
$ZnCl_2$	2600	110
$ZnBr_2$	3100	92·2
$CdCl_2$	2950	97
$CdBr_2$	3500	81·7

The iodides of zinc and cadmium are not included in the above table, since the region of absorption, as also its beginning, being intermixed with the spectrum of I_2, lose the amount of definiteness that is found in others.

We illustrate our arguments, taking the particular case of $ZnCl_2$ absorption. The spectrum observed in absorption is perfectly continuous and absolutely unassociated with any banded structure. This means that the molecule is excited with the agency of light from the normal state to another state which is an unstable one. This state is certainly not the state that corresponds with the binding energy 'R' of the molecule because R (= 151 k.cal. for $ZnCl_2$) is very much greater than the energy corresponding to the energy of the binding at the beginning of absorption, which, from Table VII, is 110 k.cals. Thus it is plain that the molecule is breaking due to an energy less than its energy of binding, apparently a paradox.

Thus we shall have to imagine a process in which there would remain the possibility of a molecule to dissociate photochemically with considerably less energy than the thermochemical energy of binding of the molecule. Dutta and Saha proposed such a process (9). They remarked that photon may act on one of the halogen atoms individually within a molecule of the type MX_n and may cause its disruption from the parent molecule. The energy for the process would be equal to the energy that the particular halogen atom possesses to remain itself attached tight with the molecule. Dutta and Saha assumed that the binding energy of the whole molecule MX_n was distributed equally amongst all the halogens, so that, for a particular individual

halogen, the energy of attachment would be n-th part of the whole energy. Therefore, to dissociate a molecule MX_n in a photochemical process, an energy of the amount R/n would be sufficient to cause the dissociation, R being the thermochemical energy of binding of the molecule. But when one goes to compare this with actual observations difficulties step in. Taking the case of $ZnCl_2$ as the model, $R/n - 151/2 = 75{\cdot}5$ k.cal. The corresponding energy in wavelengths is 3790 A. On our plates we could observe no trace of any absorption in this region. Thus, though qualitatively the assumption seems to be correct, it fails when applied quantitatively.

The next improvement in our picture would be to assume that the halogens in such molecules are attached unsymmetrically from the standpoint of the energy. This immediately leads to a dissociation equation :

$$ZnCl_2 + h\nu_1 = ZnCl + Cl \quad . \qquad . \quad (27)$$

where $(h\nu_1) = \frac{1}{2}(h\nu)$, ν being the frequency of absorption corresponding to the thermochemical energy ' R.' The potential energy curve for the molecule $ZnCl_2$ (being heteropolar, it is of the type $Zn^{++}Cl^{-}Cl^{-}$) goes down to a sharp minimum, from where it rises again. At the same time the potential energy curve for ZnCl would also be similar in nature since it is assumed that the light of the energy $h\nu_1$ acts only on one halogen, leaving the rest untouched. It is well known that a transition from one state to another that possesses a minimum in course of its potential energy curve gives rise to banded structure in the resulting spectrum. The absorption spectrum under our observation is absolutely free from any bands.

Thus we have no other alternative than to assume the following process for dissociation of a molecule with an energy less than its energy of binding. Both states, the normal and the excited, possess minima in course of their potential energy curves. They are shown in fig. 1. The course for $Zn^{++}Cl^{-}Cl^{-}$ is marked A in the figure, for $(ZnCl)^{+}\ Cl^{-}$ by ' B ' and a third state ZnClCl by ' C.' It is clear that state ' A ' is more strongly heteropolar than state ' B,' and in the case of ' C ' there exists no polarity. This means that the nuclear separation factor ' r ' at the minimum in curve ' A ' will be much smaller than that in the case of ' B,' and it will not be very unreasonable

to assume that the minimum of ' B ' lies beyond the curve ' A ' as given in fig. 65. Now from the curves it will be clear that any transition from ' A ' to ' B ' will result in the

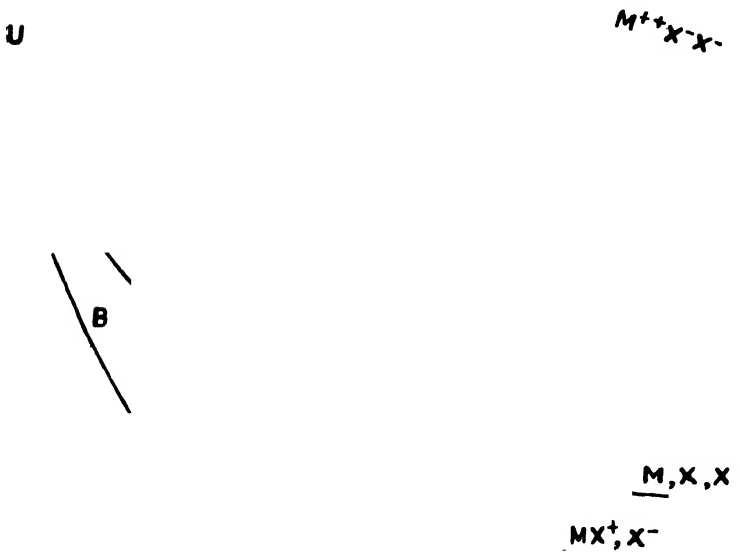

FIG. 65. Potential Energy Curves for MX_2 molecule.

dissociation of the molecule as if the transition is taking place to an unstable state, though ' B ' possesses a stable minimum.

On this ground we assume that the continuous absorption

observed in the case of $ZnCl_2$ molecule, the beginning of which lies at λ 2600, is due to the light acting on one electron only. The value in heat units for this energy, from Table VII, is 110 k.cal. This will be the value of R_1 in the following equation :

$$MX_2 + R_1 = MX + X \quad . \quad . \quad (8a)$$

In the case of $ZnCl_2$, if R_2 is given by

$$MX + R_2 = M + X \quad . \quad . \quad (9a)$$

we can write

$$R_1 + R_2 = R \quad . \quad . \quad . \quad (28)$$

So that binding energy ' R_2 ' of the molecule MX is given by

$$\begin{aligned} R_2 &= (R - R_1) \quad . \quad . \quad . \quad (29) \\ &= (151 - 110) \\ &= 41 \text{ k.cals.} \end{aligned}$$

As at present we find no other method to corroborate the value of R_2 obtained by us with that from other sources, we simply tabulate our values as derived with the help of relation (29) in the following table (Table VIII) in k.cals.

TABLE VIII

Substance	R	R_1	R_2
$ZnCl_2$	151	110	41
$ZnBr_2$	124·8	92·2	32·6
$CdCl_2$	142	97	45
$CdBr_2$	117·8	81·7	36·1

SUMMARY

The absorption spectra of zinc and cadmium halides are studied in the visible and in the ultraviolet at different temperatures and with different pressures of the gas. The vapours of these salts absorb light continuously from a long wave limit, resulting in the photochemical decomposition of

the salt into normal state in accordance with the general photochemical equation for heteropolar molecules :

$$MX_2 + h\nu = M + 2X.$$

This energy $h\nu$ corresponds with the thermochemical energy of binding of the molecules.

There were observed other regions of absorption with energy less than the thermochemical energy of binding of the molecules. These are interpreted as due to a single electron transition in the normal molecule $M^{++}X^{--}$. With this interpretation the binding energy of the temporary molecule MX is calculated.

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